STUDIES ON PREPARATION, CHARACTERIZATION AND APPLICATIONS OF NANOCOMPOSITES BASED ON CONDUCTING POLYMERS AND INORGANIC NANOPARTICLES

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CERTIFICATE

This is to certify that the work embodied in this dissertation entitled **"Studies on preparation, characterization and applications of nanocomposites based on conducting polymers and inorganic nanoparticles"** is the original contribution of **Mr. Mahfoozurrahman Khan**, carried out under my guidance and supervision and is being submitted in partial fulfilment of the requirement for the award of the degree of **Master of Philosophy** in **Applied Chemistry** from **Aligarh Muslim University, Aligarh**. This work has neither been submitted, nor is being submitted, for any other degree.

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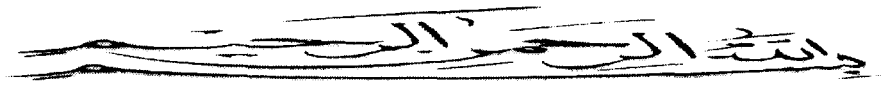

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MAHFOOZURRAHMAN KHAN

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Introduction

1. INTRODUCTION

1.1. Nanomaterials

The rise of nanotechnology from a laboratory curiosity to a multibillion dollar industry has been the most remarkable transformation seen by the technology industries in the past few years. Nanomaterials are cornerstones of the nanoscience and nanotechnology.

They include of a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in recent years. It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed.

Nanomaterials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers. For the exploration of nanomaterials, materials science-based approach to nanotechnology is undertaken. Their physical and chemical properties are expected to differ measurably than those in the bulk materials. It covers the study of materials with morphological features on the nanoscale, especially those materials that have special properties stemming from their nanoscale dimensions. **Figure 1.1** shows some basic nanomaterials available in different morphological forms.

The history of nanomaterials began immediately after the big bang when nanostructures were formed in the early meteorites [1]. Nature later evolved many other nanostructures like seashells, skeletons etc. [2]. Nanoscaled smoke particles were formed during the use of fire by early humans [3].

The scientific story of nanomaterials, however, began much later. One of the initial scientific reports is the colloidal gold particles synthesized by Michael Faraday as early as in 1857 [4]. Nanostructured catalysts have also been investigated for over 70 years. By the early 1940s, precipitated and fumed silica nanoparticles were being manufactured and sold in USA and Germany as substitutes for ultrafine carbon black for rubber reinforcement [1]. Nanosized amorphous silica particles have found large-scale applications in many every-day consumer

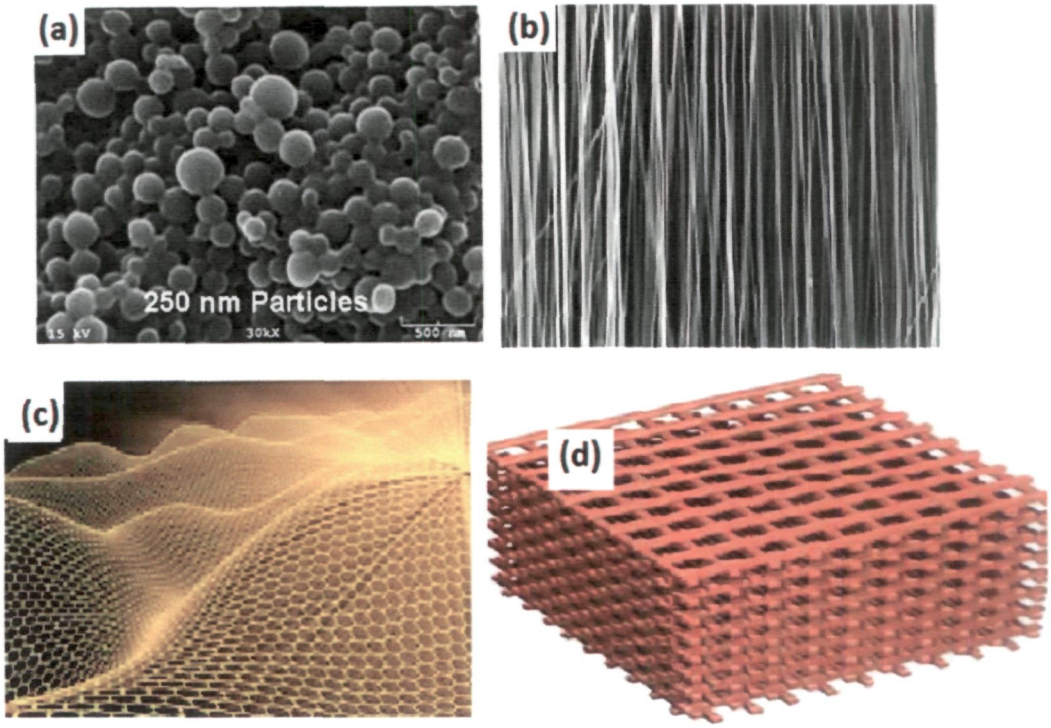


Figure 1.1. Some basic nanomaterials available in different morphological forms: (a) spheres and clusters, (b) 1D nanofibers, wires and rods, (c) 2D films, plates and networks and (d) 3D nanomaterials.

products, ranging from non-dairy coffee creamer to automobile tires, optical fibers and catalyst supports [5]. In the 1960s and 1970s metallic nanopowders for magnetic recording tapes were developed [6].

In 1976, for the first time, nanocrystals produced by the now popular inert- gas evaporation technique was published by Granqvist and Buhrman [7]. Recently, it has been found that the Maya blue paint is a nanostructured hybrid material [8]. The origin of its color and its resistance to acids and biocorrosion are still not understood but studies of authentic samples from Jaina Island show that the material is made of needle-shaped palygorskite (clay) crystals that form a superlattice with a period of 1.4 nm, with intercalates of amorphous silicate substrate containing inclusions of metal (Mg) nanoparticles. The beautiful tone of the blue color is obtained only when both these nanoparticles and the superlattices are present, as has been shown by the fabrication of synthetic samples [9].

Some nanomaterials occur naturally but of particular interest are engineered nanomaterials (EN) which are designed for and already being used in many commercial products and processes. They can be found in sunscreens, cosmetics, sporting goods, stain-resistant clothing, tires, electronics and many other everyday items and are used in medicine for purposes of diagnosis, imaging and drug delivery [10-15].

Engineered nanomaterials are designed at the molecular (nanometre) level to take advantage of their small size and novel properties which are generally not seen in their conventional bulk counterparts. Two main reasons, why materials at the nanoscale can have different properties are increased relative surface area and new quantum effects. Nanomaterials have much greater surface area to volume ratio than their conventional forms which can lead to greater chemical reactivity and affect their strength as well. Also, the quantum effects can become much more important in determining the material's properties and characteristics leading to some novel optical, electrical and magnetic behaviors at the nanoscale [16].

One important class of such nanomaterials is nanocomposites which consist of a large number of nanometric entities such as nanoparticles, nanotubes or nanosheets as filler dispersed in a more

or less ordered fashion in some sort of matrix mostly constituted by polymers. The goal to fabricate such hybrid materials is to obtain distinct properties evolved from the synergistic effects of the component materials. This may include either new or improved electronic or chemical properties that may be exploited for chemical or biological sensing or enhanced stabilities in different environments that can be utilized for energy storage and/or conversions.

Furthermore, nanocoatings and nanocomposites are finding use in diverse consumer products such as windows, sports equipment, bicycles and automobiles [17,18]. There are novel UV-blocking coatings on glass bottles which protect beverages from damage by sunlight and longer-lasting tennis balls using butylrubber/nano-clay composites [19]. Nanoscale titanium dioxide, for instance, is finding applications in cosmetics, sun-block creams and self-cleaning windows [20,21]. Silica is also being used as filler in a range of products, including cosmetics and dental fillings. It is already in commercial use, with some having been available for several years or decades. The range of commercial products available today is very broad, including stain-resistant and wrinkle-free textiles, cosmetics, sunscreens, electronics, paints and varnishes [22].

In summary, they are of tremendous interest because at this scale unique optical, magnetic, electrical and other properties emerge. The emergence of such novel properties has the potential for great impacts in electronics, medicine and other fields.

These materials have created a great interest in recent years by virtue of their unusual mechanical, electrical, optical and magnetic properties. For example:

(a) Nanophase ceramics are of particular interest because they are more ductile at elevated temperatures as compared to the coarse-grained ceramics [23-27],

(b) Nanostructured semiconductors are known to show various non-linear optical properties. Semiconductor Q-particles also show quantum confinement effects which may lead to special properties, like the luminescence in silicon powders and silicon germanium quantum dots as infrared optoelectronic devices. Nanostructured semiconductors are used as window layers in solar cells [28].

(c) Nanosized metallic powders have been used for the production of gas tight materials, dense parts and porous coatings. Cold welding properties combined with the ductility make them suitable for metal-metal bonding especially in the electronic industry [29].

(d) Single nanosized magnetic particles are mono-domains and one expects that also in magnetic nanophase materials the grains correspond with domains while boundaries on the contrary to disordered walls. Very small particles have special atomic structures with discrete electronic states which give rise to special properties in addition to the superparamagnetism behaviour. Magnetic nanocomposites have been used for mechanical force transfer (ferrofluids), for high density information storage and magnetic refrigeration [30-31].

(e) Nanostructured metal clusters and colloids of mono- or plurimetallic composition have a special impact in catalytic applications. They may serve as precursors for new type of heterogeneous catalysts (Cortex-catalysts) and have been shown to offer substantial advantages of activity, selectivity and lifetime if used in chemical transformation and electrocatalysis over traditional catalysts [32].

1.2. Conjugated Polymers

A polymer is a long chain molecule made up of many small repeating units (called monomers) which are linked together via covalent bonds. Because of their large size, they are also termed as macromolecules. The word polymer is derived from two greek words "poly" which means many and "meres" which means parts. Recently, polymer chemistry has made tremendous advances in almost all branches of science widely ranging from engineering, medical sciences to microeconomics. Polymers are classified into various groups because of vast difference in their origin, physical and chemical properties (**Figure 1.2**).

Polymers exist in countless forms and have high molecular weight. Generally, we know polymers that are plastics and behave opposite of metals. Therefore, they are used as insulators because they do not conduct electricity. Thus, the electric wires are coated with polymers to protect us from electric shocks. However, as the time passed and many new requirements came

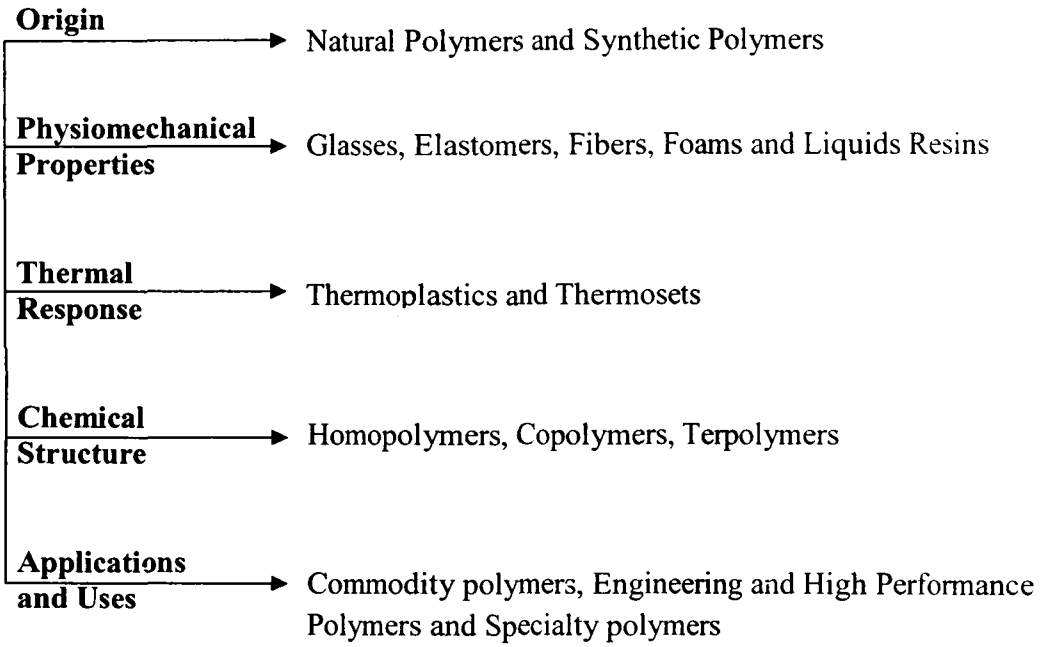


Figure 1.2. Criteria based simplified classification of polymers on the basis of origin, properties and applications.

to being, it was recognized that if the electrical conduction could be added besides several other useful properties of polymers. This led to the introduction of a new class into the organic polymers "*Electrically Conducting Polymers*". Later, sparking discovery of electrically conductive polyacetylene by Heeger, MacDiarmid and Shirakawa has revolutionized the development efforts in the field of electrically conducting polymers. For this discovery, the Royal Swedish Academy of Sciences awarded the Nobel Prize in Chemistry for the year 2000 to these three scientists.

The ability to dope these polymers over the wide range of electrical conductivity from insulator through semiconductor to metal opened a new field of research and perspective. Conjugated polymers in the doped and undoped state have an array of potential applications in the microelectronics industry including energy storage devices, sensors, sensor switchable membrane, electrochromic devices etc. [33-35].

Currently, most research efforts have focused on electrochemically driven conducting polymers actuators because they are light weight, have low operating potential and have potential applications in advanced robotics, micro-actuators and artificial muscles.

Conjugated polymers can more easily be oxidized or reduced than conventional polymers. It is because of the presence of π-conjugated structure and the electrical conduction is obtained through "doping" leading to the generation of charge-carriers in the form of free electrons or holes. The charge carriers are usually delocalized over the conjugated polymer chain [36]. The transport of the charge-carriers along a conjugated backbone can be described by the Band model as has been done for metals and semiconductors. Besides this intrachain conduction incorporating very high intrinsic conductivity to the doped conjugated polymers, several hopping and tunneling processes are also in operation for non-intrinsic (interchain and interfiber) conduction processes.

Electrical conductivities of polymers whether in the form of films or pellets can be measured using well known Ohm's law.

Resistance: $R = V/I$ Unit: Ω (Ohm)

Conductance: $C = R^{-1}$ Unit: Ω^{-1} = S (Siemens)

Resistivity: $\rho = RA/W$ Unit: Ω cm

Conductivity: $\sigma = \rho^{-1}$ Unit: $(\Omega \text{ cm})^{-1}$

$\sigma = L/RA$

V = Voltage (Volts)

I = Current (Amperes)

W = Thickness of the sample (cm)

A = Area of cross-section of sample (cm^2)

There are various theories and models to account for electronic conduction in these materials such as band model (**Figure 1.3**), hopping and percolation mechanisms (**Figure 1.4**). The band model is used very widely as it provides a basis to understand, why one material is a metal and another is an insulator? It provides a good explanation of electric conduction only in highly ordered crystalline structures. But in case of disordered amorphous system, the mobility of electrons is impeded by localized electronic states. The electronic conduction occurs by hopping over or tunneling through the potential energy gap.

Conjugated polymers have extended π-system and are extremely reactive towards chemical or electrochemical oxidation or reduction. Since these reactions are often reversible, there is some possibility to control the electrical and optical properties with a great deal of precision switching from a highly conducting state through semiconducting to insulating state [38, 39]. Thus conducting polymers can be professed as macromolecules with fully conjugated sequence of bond along the backbone which acquires a positive or negative charge by oxidation or reduction process.

The electrical conductivity depends on the number of charge carriers (electrons or holes) in the material and the mobilities of charge carriers. An inorganic semiconductor is basically neutral and do not contains any free electrons or holes. Hence, an effective way for the incorporation of charge carriers required for electrical conduction is by adding a very small amount of additives".

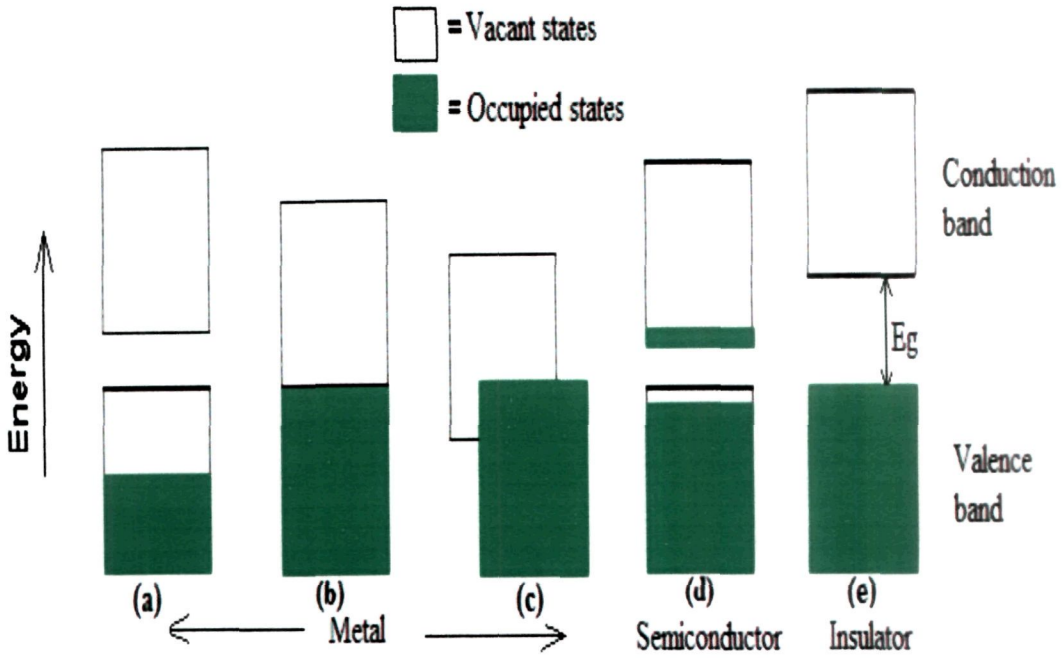


Figure 1.3. Energy band diagrams of:
Metals: (a) half filled valence band, (b) no band gap between bands and (c) overlapping bands,
Semiconductors: (d) filled or partially filled valence band or small band gap
And
Insulators: (e) full valence band with bands separated by a large band gap.

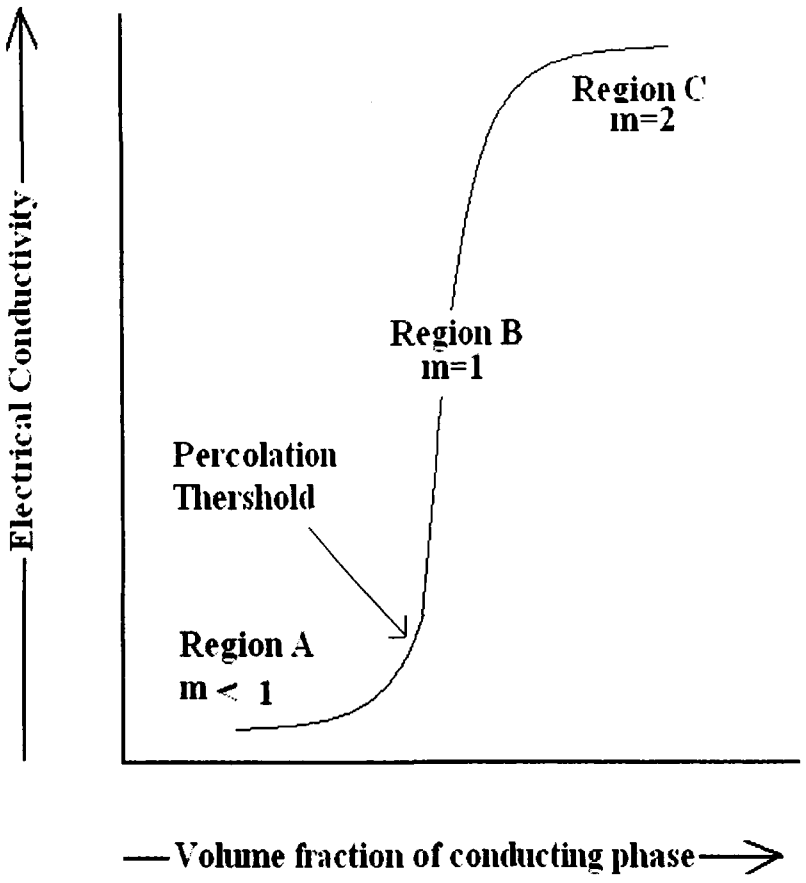


Figure 1.4. Statistical model for percolation threshold of conducting composites [37].

(in ppm). These additives are termed as "*dopant*" in (**Table 1.1**) and this process is referred to as "*doping*

The ability to undergo doping distinguishes conducting polymers from all other kind of polymers. Conducting polymers are frequently called as "*Synthetic Metals*" as well because they present electrical, electronic, optical and magnetic properties inherent to metals or semiconductors while keep the mechanical properties of conventional polymers intact. Since these materials present ease of fabrication and are of potentially low cost, their use to assemble polymeric optical devices is becoming reality. Nowadays, efforts have led to the development of devices with performance comparable to those based on inorganic semiconductors. Also, the possibility of controlling the electronic and optical properties of an organic device by tailoring the organic molecular structure permits their modification before fabrication [40].

Conducting polymers have also been investigated as active materials in other optical applications such as optocouplers, full color image sensors and lasers [41-43]. Other properties of conducting polymers also enables their use as active component in batteries, biosensors[44], drug releasing agents, gas separation membranes[45-49], electrochemical capacitors [50] and electromagnetic radiation shielding [51-53].

Out of various conjugated polymers, recently polyaniline (Pani) has captured the attention of the scientific community due to its high electrical conductivity on treatment with protonic acids and became the most investigated conducting polymer since its discovery about three decades ago. It was first prepared in 1834 and has been the subject of mild research ever since [54]. However, the conducting properties of Pani were recognized and the number of research articles dealing with this conducting polymer grew rapidly since 1980s. Pani is known for its special representation due to following unique properties such as: low cost of its monomer, ease of synthesis by chemical or electrochemical routes, high environmental stability, easy to dope by protonic acid and simple versatile redox reactions.

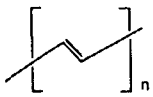
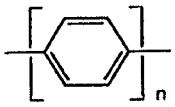
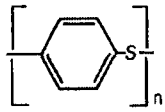
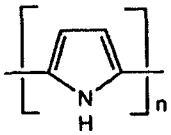
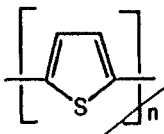
All the above mentioned features made Pani an attractive replacement material in many areas of applications such as electrodes, charge transfer and active layers, electrochromic displays,

electromagnetic shielding as well as a growth template for neurons [55-58]. Pani can be synthesized by both the chemical and electrochemical oxidative polymerization. The most common synthesis of Pani involves oxidative polymerization in which the polymerization and doping occurs concurrently and may be accomplished either electrochemically or chemically. Electrochemical methods tend to have lower yields than chemical ones [59]. Pani exists in four main oxidation states viz.: (**Figure 1.5**). ES and EB states of polyaniline.

The most common synthesis of Pani involves oxidative polymerization of aniline in which the polymerization and doping occurs concurrently and may be accomplished electrochemically or chemically. Electrochemical methods tend to have lower yields than that from chemical methods [59].

Synthesis of Pani by polymerizing aniline through chemical oxidative route in acidic medium involves the use of hydrochloric acid, nitric acid or sulfuric acid in the presence of oxidizing agent such as ammonium persulfate [$(NH_4)_2S_2O_8$], potassium persulfate [$K_2S_2O_8$] etc. in aqueous medium. The principal function of the oxidant is to withdraw a proton from an aniline molecule without forming a strong co-ordination bond either with the substrate/intermediate or with the final product. However, smaller quantity of oxidant is used to avoid oxidative degradation of the polymer formed. In the review article by Gospodinova *et al* [60-61], they had reported that the propagation of polymer chains proceed by a redox process between the growing chain (as an oxidant) and aniline molecules (as a reductant) with addition of monomer to the chain end. The high concentration of a strong oxidant, [$(NH_4)_2S_2O_8$], at the initial stage of the polymerization enables the fast oxidation of oligoanilines and Pani. This is usually performed by oxidizing the aniline and mixing them slowly to form Pani. Depending upon the required electrical conductivity of the Pani, the resulting polymer may be exposed to other chemicals in a process called doping. Doping of Pani leads to a more stable polymer that will allow it to conduct current evenly [62]. M. Hatano *et al* [63] also reported the fast oxidation of oligomers and Pani as well as their existence in the oxidized form.

Table 1.1. Structures and electrical conductivities of some doped conjugated polymers.

Conjugated Polymer	**Structure**	**Typical Method of Doping**	**Typical Electrical Conductivity (Scm^{-1})**
Polyacetylene		Electrochemical, Chemical (AsF_5, I_2, Li, K)	$500 - 1.5x10^5$
Polyphenylene		Chemical (AsF_5, Li, K)	500
Poly(phenylene sulphide)		Chemical (AsF_5)	1
Polypyrrole		Electrochemical (BF_4^-)	600
Polythiophene		Electrochemical (BF_4^-)	100

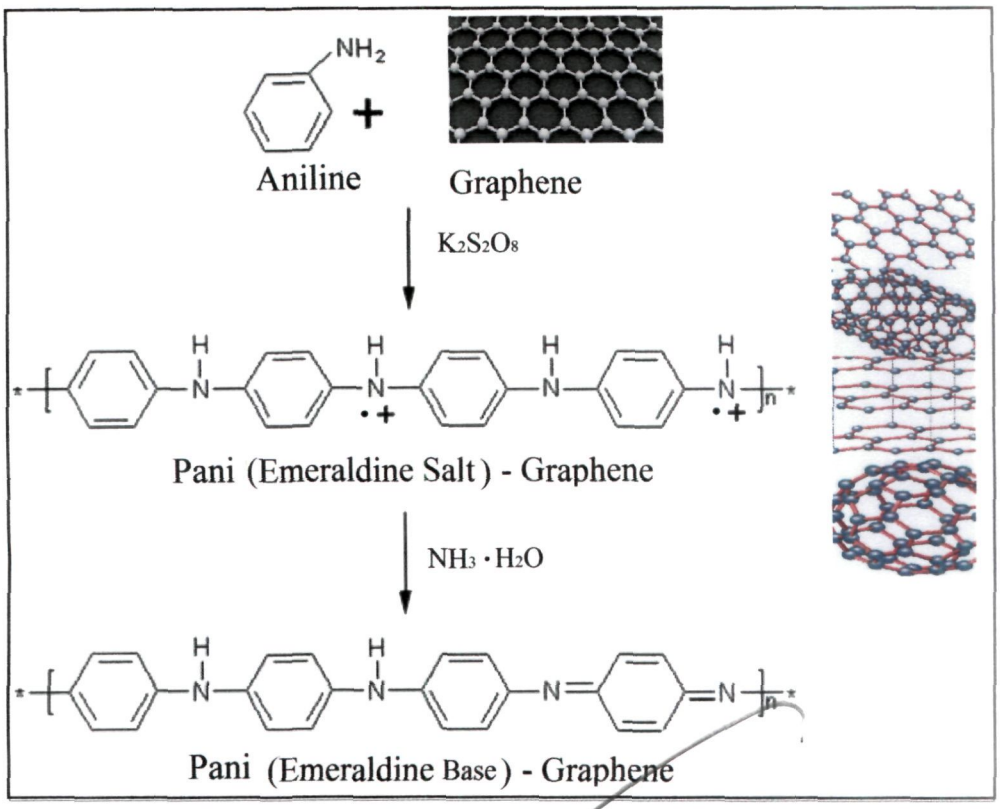


Figure 1.5. ES and EB states of polyaniline.

Electrochemical deposition is another viable approach for the preparation of Pani. The electrochemical preparation of conducting polymer dates back to early attempts of Dall'olio and coworkers [64] who obtained "*pyrrole black*" as it was called at that time on electrochemical oxidation of pyrrole in aqueous sulphuric acid in the form of highly insoluble powder on platinum electrode.

1.3. Polymer Nanocomposites

The nanocomposites are those materials that combine two or more individual components in order to improve performance/properties/characteristics greater than those of the components taken separately in which at least one dimension of the dispersed particles of a component is in the nanometer range i.e. around 10^{-7} to 10^{-9} m. They have properties that are superior to individual components and can be prepared using simple and inexpensive techniques.

The nanocomposites may be classified into the following four types depending upon the nature of dispersed phase and dispersion medium: (i) organic-organic nanocomposites (nanoparticles of organic dyes dispersed in the matrix of polymethylmethacrylate), (ii) inorganic-organic nanocomposites (metal or semiconductor nanoclusters/particles dispersed in a polymer matrix such as poly methyl methacrylate and block copolymers), (iii) organic-inorganic nanocomposites (nanoparticles of organic dyes or biopolymers dispersed in an inorganic matrix such as silica, titania or alumina) and (iv) inorganic-inorganic nanocomposites (gold nanoparticles dispersed in the matrix of silica).

The addition of small amounts of nanoparticles to the polymers has been able to generate new properties in the composite material. Polymer based nanocomposites are the polymer matrices containing nanoparticles or bunches of nanoparticles that are randomly distributed within the polymer matrices. Thus, the nanoparticles in such composites are dispersed phase while the polymer matrix as dispersion medium. Their properties are dependent on the surface treatment of the nanoparticles and processing technique used. The most important step in the preparation of polymer-based nanocomposites is the dispersion of filler in the polymer matrix.

In the non-polymer based composites, the main part of the volume is occupied by a ceramic. i.e. a chemical compound from the group of oxides, nitrides, borides, silicides etc. Ideally both the components, the metallic one and the ceramic one, are finely dispersed in each other in order to elicit the particular nanoscopic properties. Nanocomposite from these combinations were found to demonstrate the improving their optical, electrical and magnetic properties [65] as well as tribological, corrosion-resistance and other protective properties.[66] Size reduction of the components to the nanoscale causes improvement of the above mentioned properties and leads to newer application areas.

In general, the nanocomposites possess: (i) high mechanical strength stiffness toughness and tensile strength, (ii) gas, oxygen, water etc. barrier properties, (iii) good thermal stability, (iv) good chemical stability, (v) good optical clarity (since particles are of nano-size), (vi) good dimensional stability, (vii) good heat resistance and (viii) recyclability.

The primary reason for adding inorganic filler particles to polymer matrices is to improve their mechanical performance. For example, the addition of high-modulus filler increases the modulus and the strength of a polymer. Dispersed nanoparticles can improve the modulus and strength and maintain or even improve ductility because of their small size that does not create large stress concentrations [67]. Numerical simulations predict tensile moduli in the order of 1 TPa for CNTs making them perhaps the ultimate high stiffness filler material. Numerical simulations and experimental findings also suggest large elastic (recoverable) strains for nanotubes. Other forms of nanoreinforcements such as nanoclays and graphite nanoplatelets also have high modulus values for nanocomposites i.e. high stiffness enhancement. The followings aspects are also very important to be considered in relation to polymer nanocomposite formulation.

Multifunctionality: The materials may be designed to mechanical requirements besides some other secondary material properties. For example, low volume (weight) fractions of nano-reinforcement have been used to enhance the electrical conductivity, to increase the working temperature and to improve the barrier and diffusion properties of polymers (primarily for platelet-shaped reinforcement) besides improving the mechanical properties.

Electrical and Optical Properties: This becomes particularly important because of the possibility of creating composites of unique combinations of functionalities such as electrically conducting composites with good wear resistance that are optically clear as well. Optical composites have been defined as composites consisting of optically active nanoparticles embedded in a transparent host material often a polymer.Optical properties of materials that are difficult to grow in the form of single crystals or that require protection from the environment and give them the ease of processing afforded by many polymers. In addition, nanoscale particles are required to achieve specific optical properties in materials for some specific applications while the role of polymer matrix is just to hold the particles together and to provide processibility. For example, high-grade optical composites of properties otherwise obtainable only in optical glasses became accessible through the use of polymer molding techniques [67].

Reinforcement: The nanoparticle reinforcement of polymers were inconsistent with respect to the changes in fundamental thermal and mechanical properties of the resultant nanocomposites. arrangement of nanoparticles, nanoscale mechanical response of the nanoparticles the chemical modification of the nanoparticles etc. Initially, the most significant factor was nanoparticle dispersion where reducing nanoparticle clustering led to the better dispersion and increased the surface area of contact between polymer and nanoparticles.

Despite of numerous challenges, considerable research has been done to develop appropriate synthetic techniques for making good polymeric nanocomposites as evident from the literature.

1.4. Preparation of nanocomposites

There are several ways of dispersing nanoparticles in polymer matrix. Few of them are discussed below [67].

Direct/melt mixing: In this method prepration of nanocomposite involves mechanically blending organically modified inorganic nanoparticles with polymer matrix [68]. No solvents are required during the processing of this method for example, polypropylene and nanoscale silica have been mixed successfully in a two-roll mill but the samples with more than 20 wt. %

of filler could not be drawn. Melt mixing is the fastest method of low capital costs due to its compatibility with existing processes . Polymer processing equipments include extruders or injectors. **Figure.1.6 (a)** presents a simple flow diagram for the melt mixing process.

Solution mixing: This is a very simple method that involves the dispersion of nanoparticles in solution of polymer followed by drying of the solvent. This method is relatively easy and commercially available nanoparticles can be used for preparation of nanocomposites by this method. **Figure 1.6 (b)** gives an idea of producing nanocomposites by solution mixing process. Special care has to be taken to avoid flocculation or agglomeration.

***In-situ* polymerization:** *In-situ* polymerization method is also a very useful method for the preparation of high performance polymer nanocomposites containing inorganic nanoparticles. In this method, nanocomposites are prepared from the suspension of monomer molecules and organically modified nanoparticles and then effecting polymerization *in-situ* [69] by standard polymerization methods as described in **Figure 1.7 (a)**.

Emulsion polymerization: Emulsion polymerization for the preparation of polymer nanocomposites [70] involves the addition of surfactant along with inorganic nanoparticles along with monomer and initiator. Emulsion polymerization proceeds rapidly and the reaction mixture is cooled to room temperature. The final product is obtained after filtration and washing several times with distilled water. It is then dried under reduced pressure. A flow diagram for emulsion polymerization technique is shown in **Figure 1.7 (b).**

1.5. Degradation and Stability of Polymer Nanocomposites

Degradation is an irreversible change, similar to the phenomenon of corrosion of metals. Chemical degradation of any polymer is a very important phenomenon, because it affects the performance of all the polymeric materials during their applications. In practice, any change in the polymer structure or properties relative to the initial structure or initial desirable properties is called "*polymer degradation*". Thus the degradation is a generic term for any number of reactions that are possible in a polymer leading to the loss of some of its desirable properties [71].Therefore, degradation of polymers involves several physical and/or chemical processes

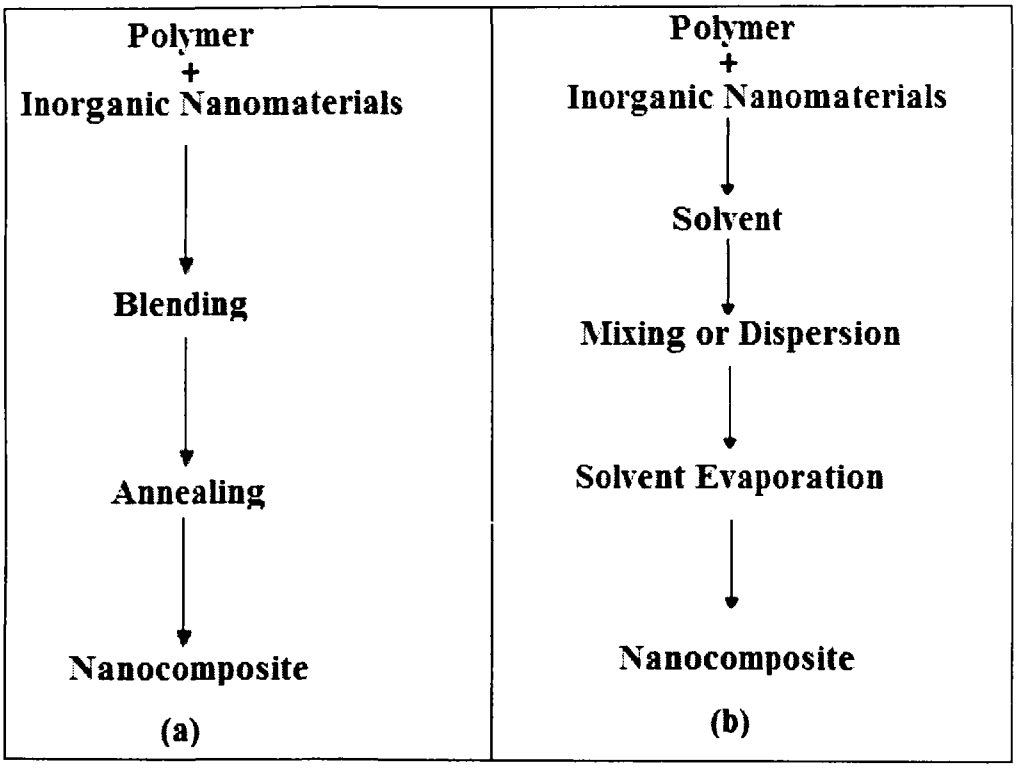


Figure 1.6. Flow diagrams for the preparation of polymer nanocomposites by: (a) melt/mixing process and (b) by solution mixing process.

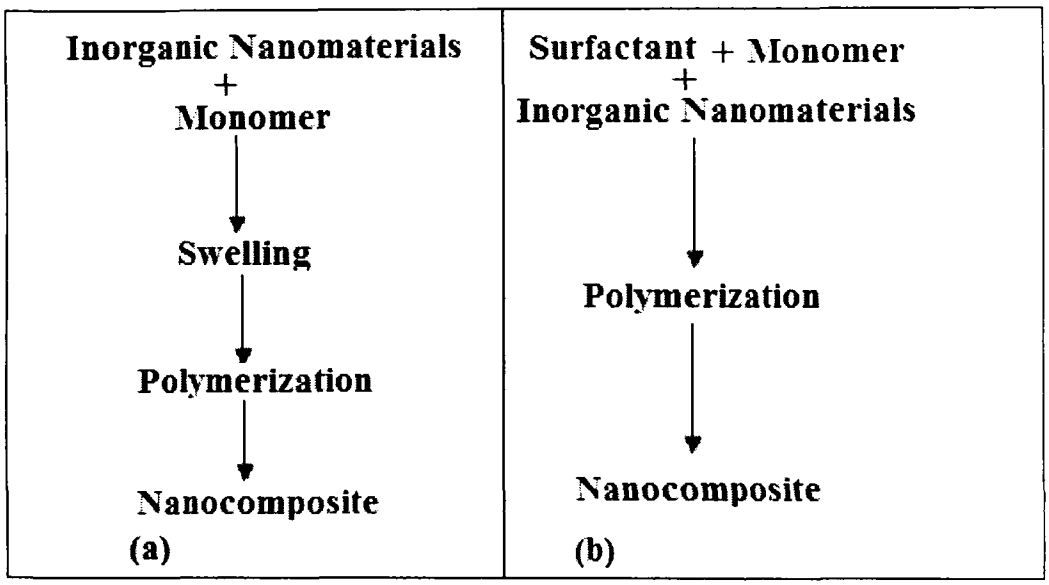


Figure.1.7. Flow diagrams for the preparation of nanocomposites by:
(a) *in-situ* polymerization and (b) emulsion polymerization process.

accompanied by small structural changes which lead to significant deterioration of the quality of the polymeric materials and finally to the loosening of its functionality and the required properties [72].

There are many external causes of deterioration of polymeric materials such as heat, light, mechanical stress, oxygen, ozone, atmospheric pollutants etc. along with other factors effective at the time of processing. Also, the presence of reactive sites in the polymer (e.g. superoxide, defects, chemically reactive groups etc.) may degrade the polymer properties with or without combination of external factors [73]. Knowledge of mechanism of polymer degradation has led to the development of more efficient polymer stabilizers [74] for high performance products on one hand and the development of sensitizers to produce environmental friendly degradable plastics [75] on the other. Sunlight consists of IR and visible radiations, apart from high energy UV radiation (200-380 nm) of the electromagnetic spectrum. The conjugated bonds, present in conducting polymers, undergo n-π^*, π-π^* and σ-σ^* transition very easily, leading to the formation of free radicals on exposure to sunlight. The UV radiation contains enough energy to cause C-C, C-N and C-O homolytic bond fission. Thus produced free radicals can react with atmospheric oxygen leading to oxidation accompanied by depletion of chain length of the polymer. The long conjugated backbone of conducting polymers could sustain defects such as free radicals. Such states can readily be oxidized.

The ability of a polymer to retain its useful properties in service is defined as the stability and the preventive measures undertaken to inhibit the degradation processes, are collectively known as "*polymer stabilization*". For the purpose of increasing durability of polymeric materials to protect from environmental factors or to reduce the rate of degradation process, the substances called "*stabilizers*" can be incorporated into polymer matrix. The degradation of conducting polymer electrode materials leads to instability in electrode potential with time. The various techniques used in the study of degradation of polymers are given in **Figure 1.8**.

1.6. Applications of Polymer Nanocomposites

The number of applications of nanocomposites has been growing at a rapid rate. The worldwide production is estimated to exceed 600,000 tonnes and is set to cover the following

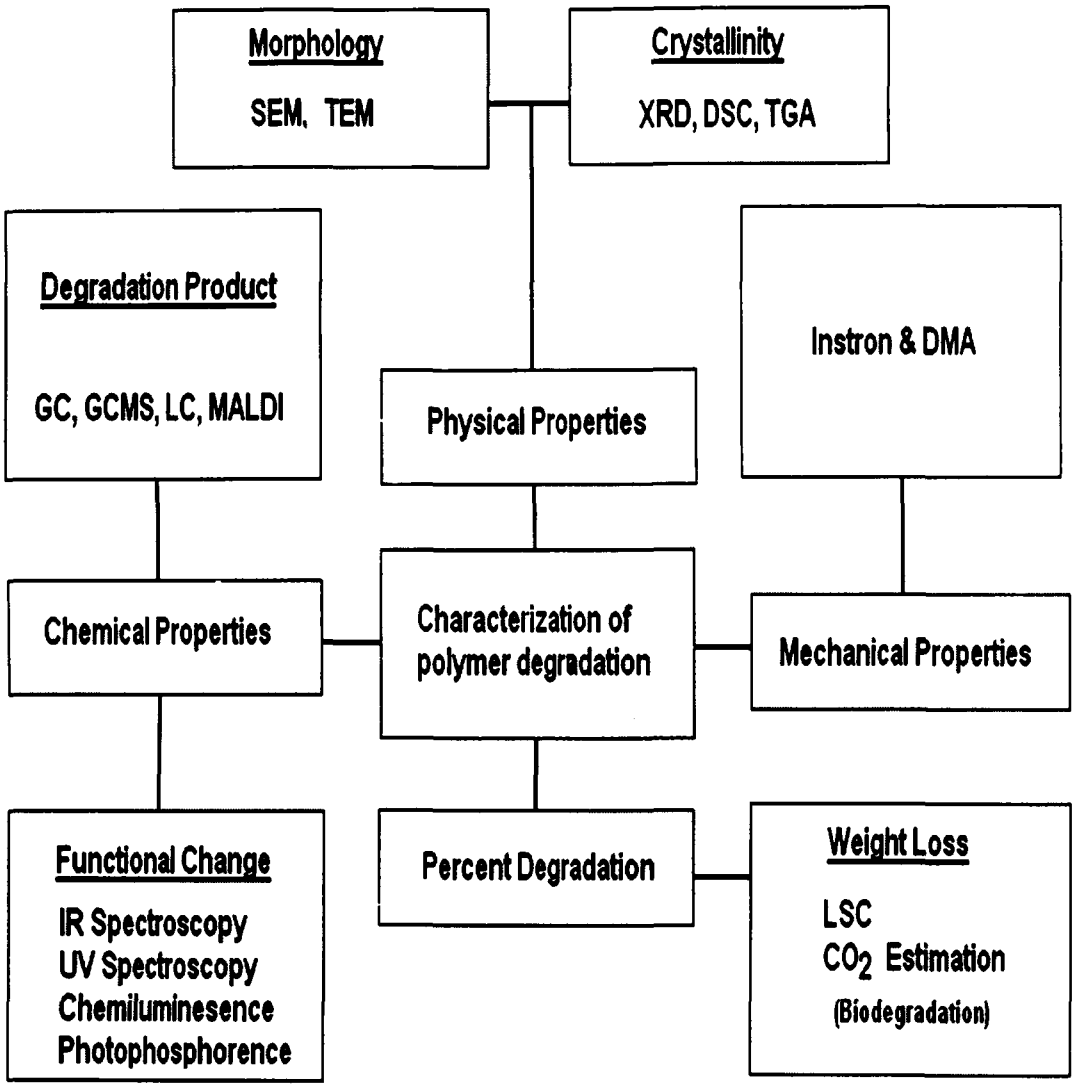


Figure1.8. The techniques commonly used in the study of polymer degradation [72].

key areas in the next five to ten years [76]. Applications could be as diverse from biological implant materials through electronic packages to automotive and aircraft components. A few of them may include: drug delivery systems, anti-corrosion barrier coatings, uv protection gels, lubricants and scratch free paint, new fire retardant materials, new scratch/abrasion resistant materials and so on [77-78]. Some very specialized applications of the polymer nanocomposites are presented further.

In batteries with greater power output: Researchers have developed a method to make anodes for lithium ion batteries from a composite formed with silicon nanospheres and carbon nanoparticles. The anodes made of the silicon-carbon nanocomposite make closer contact with the lithium electrolyte which allows faster charging or discharging of the batteries [79].

In speeding up the healing process for broken bones: Researchers have shown that growth of replacement bone is speeded up when a nanotube-polymer nanocomposite is placed as a kind of scaffold which guides growth of replacement bone. The researchers are conducting studies to better understand how this nanocomposite increases bone growth [80].

In high strength-to-weight ratio composites: Researchers have found that adding graphene to epoxy composites may result into stronger/stiffer components than epoxy composites using a similar weight of carbon nanotubes. Graphene appears to bond better to the polymers in the epoxy allowing a more effective coupling of the graphene into the structure of the composite. This property could result into the manufacture of components with higher strength-to-weight ratios for such uses as windmill blades or aircraft components.

In lightweight sensors: A polymer-nanotube nanocomposite conducts electricity very well. How well it conducts depends upon the spacing of the nanotubes. This property allows patches of polymer-nanotube nanocomposite to act as stress sensors on windmill blades. When strong wind gusts, it bends the blades. Bending changes the nanocomposite sensor's electrical conductance, causing an alarm to sound. This alarm would allow the windmill to be shut down before excessive damage occurs. Polymer semiconductor nanocomposites offer the promise of a new generation of hybrid materials with numerous possibilities of applications such as in optical

displays, catalysis, photovoltaics, gas sensors, electrical devices, mechanics, photoconductors and superconductor devices [81].

In flexible batteries: A nanocomposite of cellulossic materials and nanotubes could be used to make a conductive paper. When this conductive paper is soaked in an electrolyte, electrodes for flexible battery could be formed [82].

In removal of tumors: Now days, researchers are trying to join magnetic nanoparticles and fluorescent nanoparticles in a nanocomposite particle that is both magnetic and fluorescent. The magnetic property of the nanocomposite particle makes the tumor more visible during an MRI that is prior to surgery. Fluorescent property of the nanocomposite materials could help the surgeon to better see the tumor during operating the same [83].

In packaging: Advantages of nanocomposite films for application in the packaging industry whose main role is to improve mechanical and barrier properties of polymers, thus providing "active" or "smart" properties to packaging systems [84].

Chapter –2

Experimental

2. EXPERIMENTAL

2.1. Materials and Chemicals

Aniline from E-Merck India Ltd. was purified by distilling twice before use and graphene (GN) used in this study was purchased from Iljin Nano Tech, Seoul, Korea. Dodecyl-benzene-sulfonic-acid (DBSA) was purchased from Himedia Laboratories Pvt. Ltd., Mumbai, India. LR grade N-Cetyl-N,N,N-trimethylammonium bromide (CTAB), Potassium persulphate (PPS), HCl (AR grade), H_2SO_4, HNO_3, H_3PO_4 and methanol were purchased from CDH India Ltd. and used as received. The water used in these experiments was double distilled.

2.2. Preparation of Nanocomposites

Pani@GN nanocomposite was prepared by *in-situ* oxidative polymerization of aniline in presence of GN nanoplatelets using PPS as an oxidant. In this experiment, 0.15 g GN in 250 mL 1M HCl was ultrasonicated for 4-5 h at ~55°C. In another flask, 10 mL aniline in 500 mL 1M HCl was taken and the ultrasonicated GN suspension was added to it and stirred for 30 min. Then the 15g PPS dissolved in 250 mL 1M HCl is added slowly into the aniline/GN suspension. The reaction mixture was left under stirring for 18 h and then filtered, washed with excess water and methanol to remove PPS, HCl and Pani oligomers. Thus prepared Pani@GN nanocomposite was undoped by treating with 500 mL 1M ammonia solution. The undoped material was thoroughly washed with distilled water followed by methanol and dried at 50-60°C. Pani was also prepared using the same method as described above without the incorporation of GN. The technique used in this experiment is already reported elsewhere [1].

Thus prepared 0.75g each of Pani and Pani@GN nanocomposite was redoped with different acids: 50 mL each of 1M HCl, 1M H_2SO_4, 1M HNO_3 and 1M H_3PO_4 for 24 h, filtered and then each sample was washed with 20 mL methanol. The redoped Pani@GN nanocomposite was dried at 50-60°C for 18 h in oven.

The differently redoped Pani@GN nanocomposites were converted to fine powders and were pressed into pellets by using a hydraulic press under 37KN pressure for 10 minutes in KBr die.

Pellets were stored in desiccator for further studies. The pellets of Pure Pani were also prepared similarly.

In another experiment, the nanocomposite of Pani@GN was prepared in the presence of CTAB by *in-situ* oxidative polymerization of aniline in the presence of different amounts of GN using potassium persulphate as an oxidizing agent. Required amount of GN nanoparticles as given in **Table 2.1** was ultrasonicated for 2 h before pouring it into the aniline solution. Polymerization was effected by the addition of potassium persulphate solution. The molar ratio of aniline:CTAB:oxidant was kept 1:1:0.5 in all the experiments. The resultant mixture was kept under continuous stirring for 20 h which later turned into greenish black slurry and was filtered. Thus prepared materials were washed thoroughly with double distilled water, with methanol to remove excess of acid, potassium persulphate and polyaniline oligomers until filtrate became colorless. The nanocomposites containing different amounts of GN nanoparticles were dedoped by treating with 500 ml of 1M aqueous ammonia solution. The Pani and Pani@GN nanocomposites were redoped with 1M DBSA solution for whole night, filtered, washed with distilled water and dried at 70-80°C for 20 h in an air oven. The materials were converted into fine powders and were stored in desiccator for further investigations. The characterization of these nanocmposites is in progress and will not be reported here.

2.3. Characterization of Nanocomposites

Fourier Transform Infrared (FTIR) Spectroscopy: Fourier transforms infrared (FTIR) spectroscopy is one of the most important and emerging tool used for analyzing for different quality parameters. This technique is rapid and sensitive with a great variety of sampling techniques. Samples may be analyzed for physical, chemical and rheological properties by this technique. The FTIR spectra of selected samples were recorded using the Perkin-Elmer 1725 FTIR spectrometer.

Scanning Electron Microscopy: SEM studies were performed by using JEOL 840A to examine the surface morphology, the shape and size of the particles of selected nanocomposite samples.

Table.2.1. Preparation details of Pani@GN nanocomposites.

Sample I.D.	**Volume of Aniline (ml)**	**Weight of $K_2S_2O_8$ (g)**	**Weight of DBSA Surfactant (g)**	**Weight of CTAB (g)**	**Weight of GN (g)**
Pani	10	15.0	19.0	40.0	0.00
Pani/GN-1	10	15.0	19.0	40.0	0.1
Pani/ GN -2	10	15.0	19.0	40.0	0.2
Pani/ GN -3	10	15.0	19.0	40.0	0.3

Transmission Electron Microscopy: Transmission electron microscopes are scientific instruments that use a beam of highly energetic electrons to examine material's samples on a very fine scale. This examination can yield the information about the topography (surface features of a material's samples), morphology (shape and size of the material's particles) and elemental composition of a material's samples. Selected samples of GN, PANI and composites were observed under transmission microscope. TEM studies of the samples were done using LEO 435-VF TEM instrument.

X-Ray Diffraction (XRD) Studies:XRD is a nondestructive technique to identify crystalline phases and orientation, structural properties, grain size, phase composition, thermal expansion etc. Powder X-ray diffraction patterns of selected nanocomposite samples were obtained using 86 Bruker D8 diffractometer with Cu Kα radiation at 1.540 A° in the range of $10^{o} \leq 2\theta \leq 90^{o}$ at 40 kV.

Diffused Reflectance Spectroscopy: The UV-VIS-NIR spectrophotometer (VARIAN, Cary 5000 USA) was used to record the diffused reflectance spectra (DRS) of some selected nanocomposite samples.

Thermo-Oxidative Stability and Thermogravimetric Studies: Thermogravimetric analysis (TGA) is an analytical technique used to determine material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs as the specimen is heated. The measurement is normally carried out in air or in an inert atmosphere such as helium or argon and the weight is recorded as a function of increasing temperature. Thermogravimetric analysis of selected samples was done at a heating rate of 20°C min^{-1} in the presence of nitrogen at the flow rate 35 ml/min by DTG-60H Shimadzu TGA instrument.

DC Electrical Conductivity Measurements: The stability of Pani and Pani@GN nanocomposites was studied in terms of DC electrical conductivity retention under isothermal and cyclic accelerated ageing conditions. In isothermal experiment, Pani and the nanocomposites were heated at 50, 70, 90, 110 and 130°C and the electrical conductivity measurements were done at an interval of 10 minutes in the accelerated ageing experiments. In cyclic experiment, the

electrical conductivity of Pani and the nanocomposites was measured in the temperature range 40-150°C repeatedly for five times at an interval of 45 minutes.

The relative electrical conductivity (for isothermal and cyclic) was calculated by dividing the electrical conductivities by the initial electrical conductivity for each cycle (in case of cyclic) or for that particular temperature (in case of isothermal).

DC electrical conductivity of the doped nanocomposite pellets was measured with increasing temperature from 40°C to 150°C using a four-in-line probe DC Electrical Conductivity Measuring Instrument (Scientific Equipments, Roorkee, India). DC electrical conductivity (σ) was calculated using the following equations:

$$\sigma = [\ln 2(2S/W)]/[2\pi S(V/I)] \quad (1)$$

where I, V, W and S are the current (A), voltage (V), thickness of the film (cm) and probe spacing (cm) respectively and σ is the conductivity (S/cm) [2].

Thermal Stability of the Nanocomposites in Terms of DC Electrical Conductivity Retention: The thermal stability in terms of DC electrical conductivity retention for various samples was studied by two different techniques, which are discussed below [3]:

The thermal stability of the composite films in terms of DC electrical conductivity retention was studied by repeatedly measuring DC electrical conductivity using four-in-line probe technique for DC electrical conductivity measuring instrument. Each sample was studied for five cycles by repeatedly heating and cooling at an interval of 1 hour with cycling temperature between 40°C and 150°C.

The thermal stability of the nanocomposite samples in terms of DC electrical conductivity retention was also studied under isothermal conditions by using four-in-line DC electrical conductivity measuring instrument. This study of all the samples were carried out at 50°C, 70°C, 90°C, 110°C and 130°C under the accelerated ageing conditions. The electrical conductivity

measurements were done at an interval of 10 min. for an hour. The obtained data were plotted for relative DC conductivity (σ/σ°) versus time to study the isothermal stability in terms of DC electrical conductivity retention of the samples.

Chapter –3

Results and Discussion

3. RESULTS AND DISCUSSION

3.1. Preparation of Materials

Pani and Pani@GN nanocomposites were prepared via *in-situ* oxidative polymerization technique by doping them with different acids to render them conductive. The protons and the counterion of doping acids influence redox properties of the Pani. The doping phenomenon is governed by the principle of charge electroneutrality and the incorporation of positive charges on the Pani backbone (p-type doping due to incorporations of proton) while negative counterion remains around as the oxidation state of the polymer is changed. Thus depending on the degree of protonation and nature of counterion, the doping with different acids would lead to Pani of different redox properties [1].

A scheme showing proton doping phenomenon is represented in **Figure 3.1**.

3.2. Characterization

X-ray Diffraction (XRD) Studies: X-ray diffraction (**Figure 3.2**) of Pani showed a single broad amorphous peak for Pani at $2\theta = 19.5°$, due to the periodicity parallel to the polymer chain [2]. In the case of Pani@GNnanocomposite an additional sharp peak at $2\theta = 26.5°$ that may be assigned to graphene with a typical *d*-spacing of 0.33 nm. The other smaller peaks at higher 2θ (44, 55, 77 and 84°) are present which are also indicative of the presence of GN in the nanocomposite [2, 3].

This indicates that GN was successfully incorporated into Pani matrix for successful translation of properties of both the constituents into Pani@GN nanocomposite.

Scanning Electron Microscopy (SEM) Studies: The surface morphology of Pani and Pani@GN nanocomposite was analyzed by FESEM at different magnifications as presented in **Figure 3.3**. In case of Pani, agglomerated nanofibrous structures may be seen at lower magnification whereas highly ordered arrangement of nanofibrous structures may be observed at higher magnification.

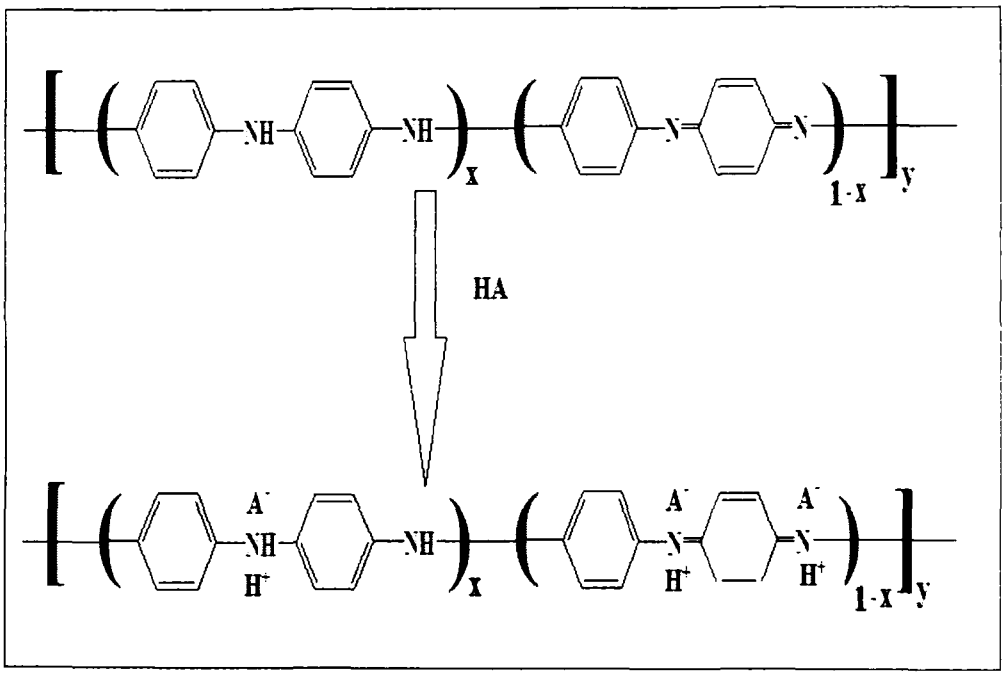


Figure 3.1. Doping of Pani (Emeraldine Base) with protonic acid (H = proton and A = counterion).

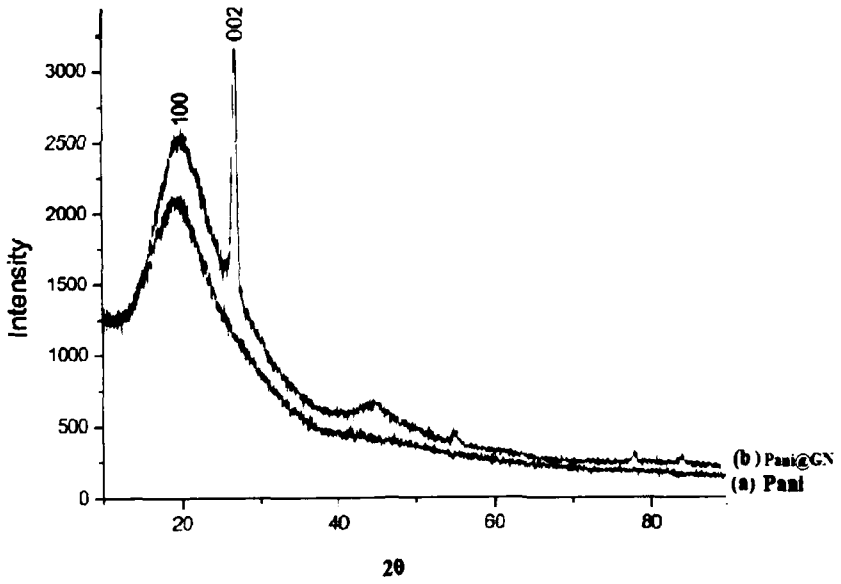


Figure 3.2. XRD spectra of Pani and Pani@GN nanocomposite.

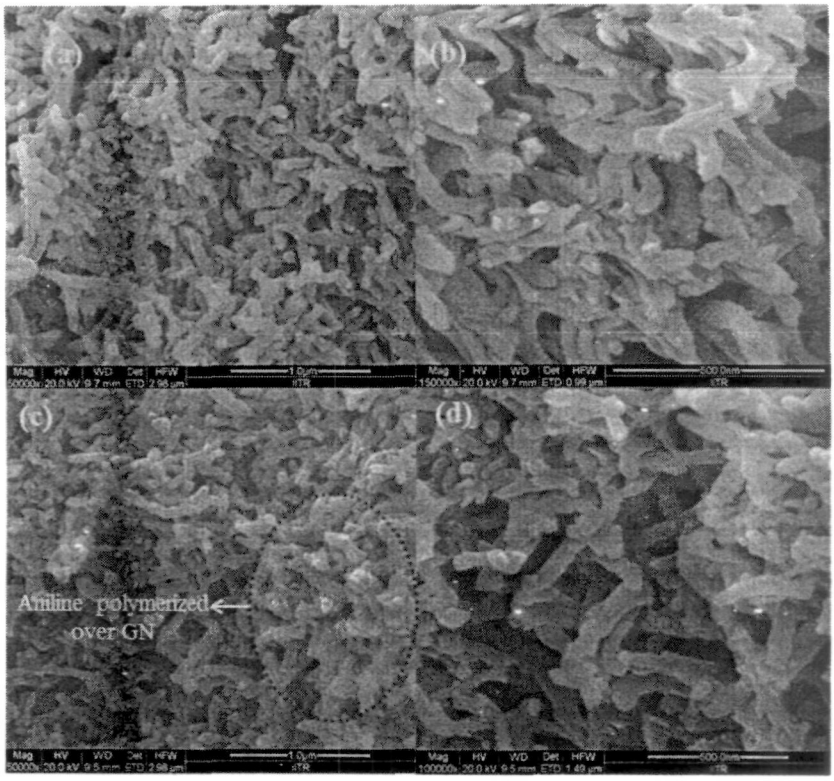


Figure 3.3. SEM of: Pani (a) and (b) and Pani@GN nanocomposite (c) and (d) at different magnifications.

Huang *et al* [3] explained on the basis of their observations that nanofibers formation is the intrinsic property of Pani and no template or structural directing agents are required. The formation of one dimensional structure in our case may be explained on the theory of rapid mixing of acidic solution of oxidant with the acidic solution of aniline monomer. As soon as the oxidant solution is mixed, the polymerization of aniline takes place and the small chains of Pani act as templates on which adsorption of aniline monomer and their subsequent polymerization occurs. However, in this case of rapid mixing method, the PPS is consumed at the onset of polymerization, hence secondary growth of Pani is limited resulting in the formation of nanofibers [4].

In case of Pani@GN nanocomposite, similar morphology is observed due to similar synthetic conditions, the aniline is adsorbed on the surface of GN and is subsequently polymerized. The growth of Pani on GN surface is difficult to observe due to comparatively much smaller dimension of GN nanoplatelets (~8 nm x ~500 nm) [5]. A schematic representation of the formation of nanofibrous morphology scheme is given in **Figure 3.4.**

Transmission Electron Micrograph (TEM): The tubular morphology of Pani may be seen in the micrograph presented in **Figure 3.5**. The length of individual nanofibers varied to several hundreds of micrometer while the thickness was less than 100 nm suggesting that they may be classified in the nanofibers.

FTIR Spectroscopy: The FTIR spectra of Pani and Pani@GN nanocomposite are shown in **Figure 3.6**. The characteristic peaks of Pani were observed at 3232 and 3024 cm^{-1} which can be attributed to the free (non-hydrogen bonded) N–H stretching vibration and asymmetric stretching of –CH respectively. The peak at 1591 cm^{-1} is due to C=C stretching mode of the quinoid rings, 1496 cm^{-1} due to C=C stretching mode of benzenoid rings and the peak at about 1303 cm^{-1} may be related to the C–N stretching mode. The peak at 829 cm^{-1} is usually assigned to an out-of-plane bending vibration of C–H of 1,4-disubstituted benzenoid rings which also confirms the formation of Pani. The characteristic absorption peaks of Pani were found at 3470, 3024, 1590, 1496, 1304 and 829 cm^{-1} in Pani@GN composite.

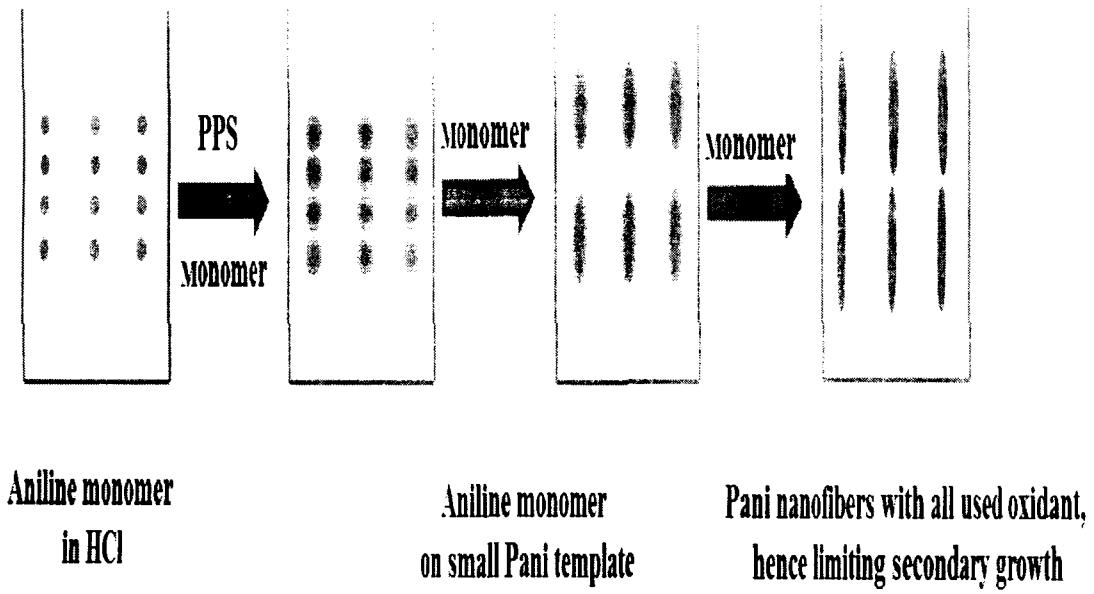


Figure 3.4. Schematic representation of formation of Pani fibers on Pani template.

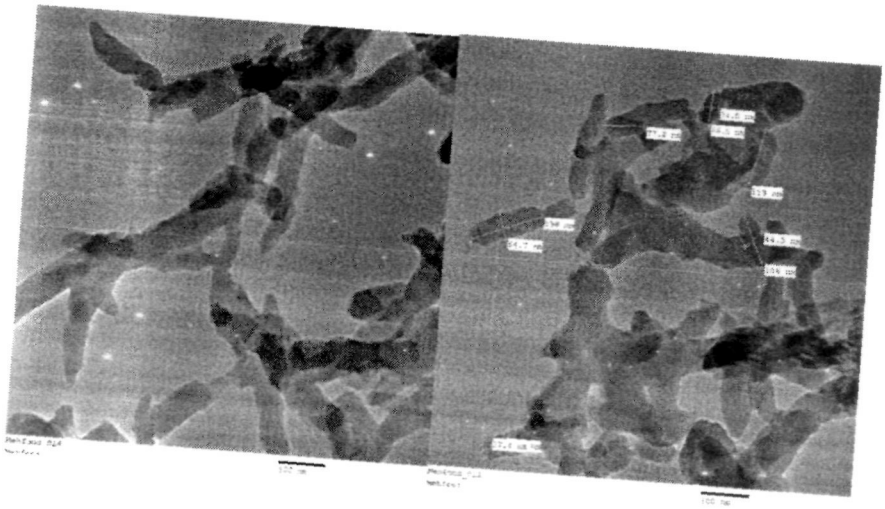


Figure 3.5. TEM of Pani.

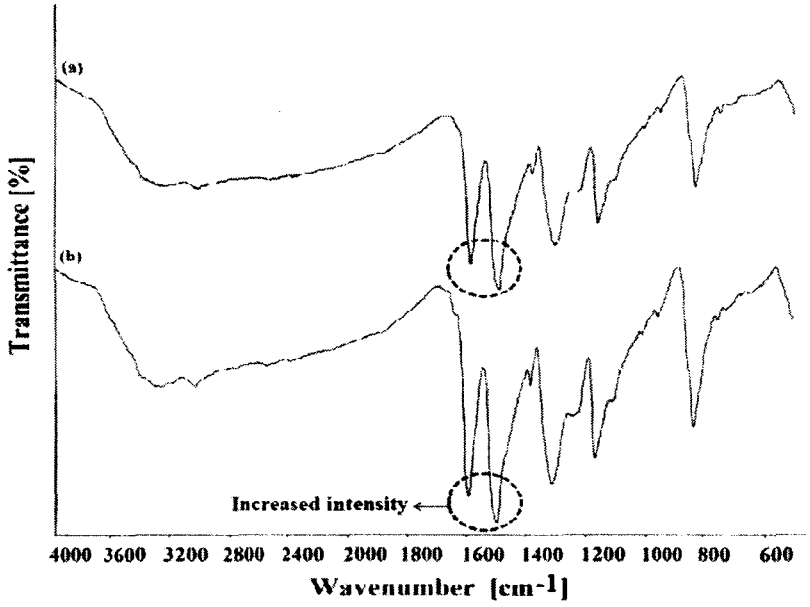


Figure 3.6. FTIR spectra of: (a) Pani (EB) and (b) Pani@GN (EB) nanocomposite.

Thus in Pani@GN composite, no additional absorption peak of GN was observed. However, as compared to Pani, an increase in the intensity of quinoid and benzenoid structures is observed in Pani@GN nanocomposite suggesting a π-π interaction between GN and conjugated structure of Pani [6]. This π-π interaction may facilitate the transfer of charge carriers hence improving the conductivity.

Diffused Reflectance Spectroscopy: Thus prepared Pani and Pani@GN nanocomposite showed high absorption in the UV-visible region with some extension in the near IR region. The UV-visible spectra showed three absorbance peaks at λ = 280, 470 and a large broad peak in the range of ~600-750 nm which originated from π–π* transition of the benzenoid rings, the polaron–π* transition and π–polaron transition respectively. The peak changed to sharp peak at ~660 nm in the case of HCl doped Pani which is indicative of the presence of protonated Pani in the prepared nanocomposites **Figure 3.7**.

In the case of Pani@GN nanocomposite (EB) nanocomposite the absorbtion around ~ 280 nm is much increased suggesting the possibility of π–π* transition between Pani and GN. While in the case of HCl doped Pani@GN nanocomposite, the absorption related to π–π* transition of the benzenoid rings, the polaron–π* transition and π–polaron transition are much higher suggesting the doped nature of Pani@GN nanocomposite.

DC Electrical Conductivity: The DC electrical conductivity of Pani was found to be dependent on the type of doping acid used as well as on absence and presence of GN nanoplatelets. From the electrical conductivity measured at all the samples, it may be concluded that all as prepared materials are semiconducting in nature.

The initial electrical conductivity of acid doped as-prepared Pani is shown in **Figure 3.8**. The electrical conductivity of differently doped materials follows the order of H_2SO_4>HCl>HNO_3 >H_3PO_4 in case of Pani. In case of Pani@GN nanocomposite, the electrical conductivity follows the same trends as shown in **Figure 3.9**. The extent of enhancement of electrical conductivity of Pani on incorporation of GN follows the order of H_2SO_4>HNO_3>H_3PO_4>HCl as shown in **Figure 3.10**.

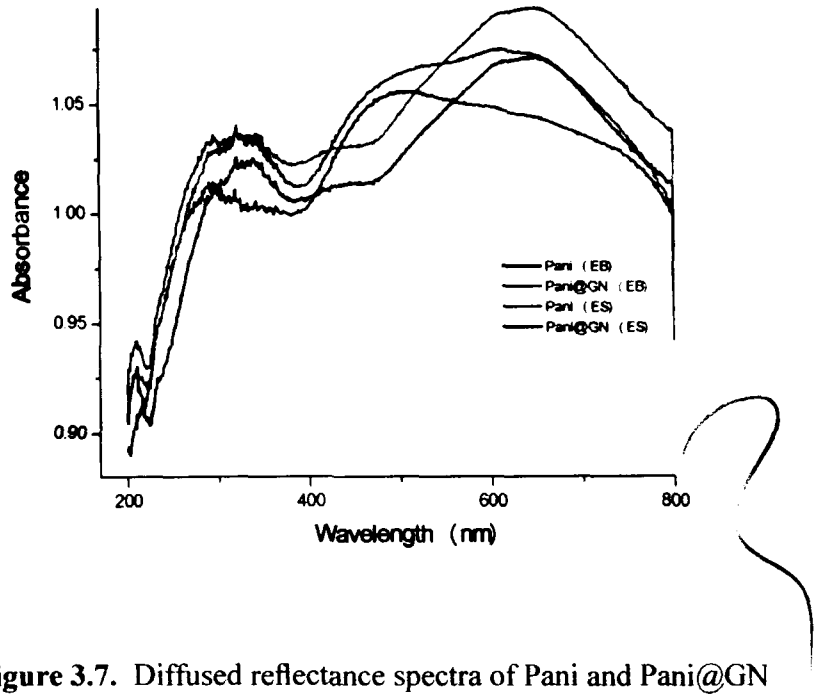


Figure 3.7. Diffused reflectance spectra of Pani and Pani@GN nanocomposite.

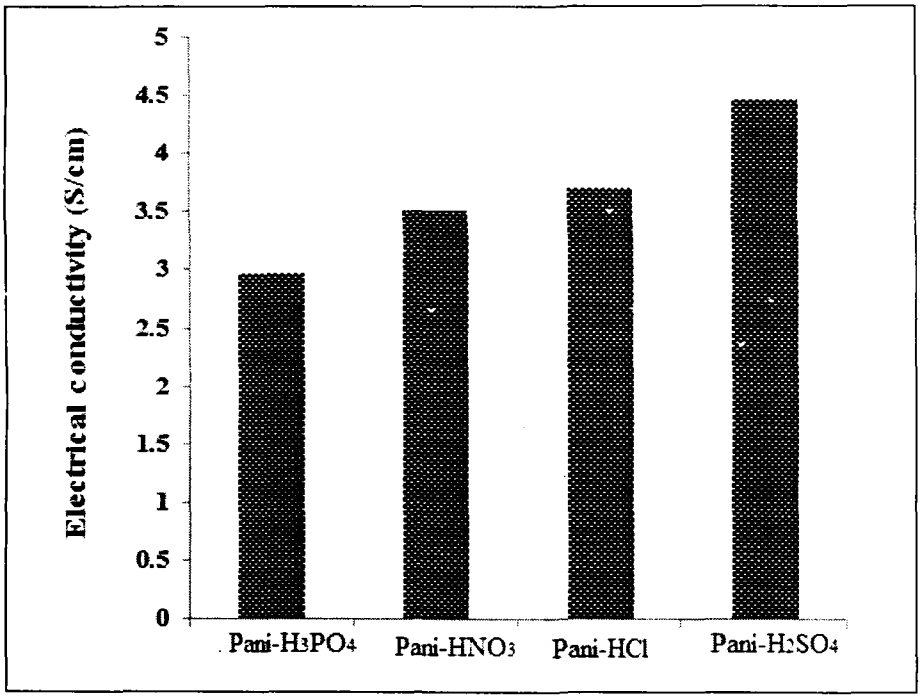


Figure 3.8. Initial electrical conductivity of Pani doped with different acids.

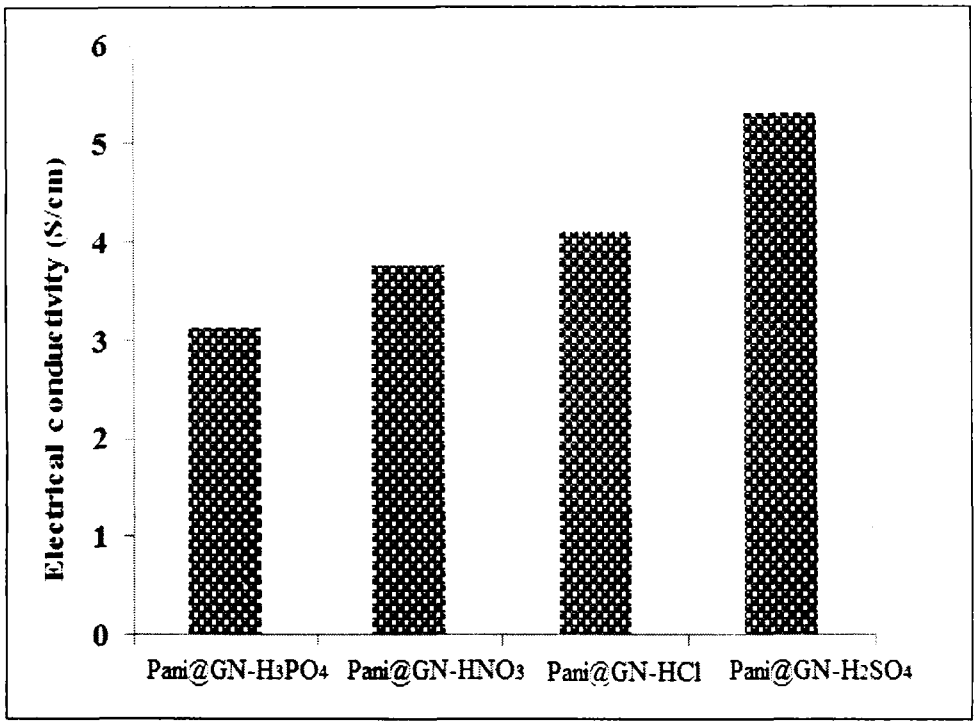


Figure 3.9. Initial conductivity of Pani@GN nanocomposite doped with different acids .

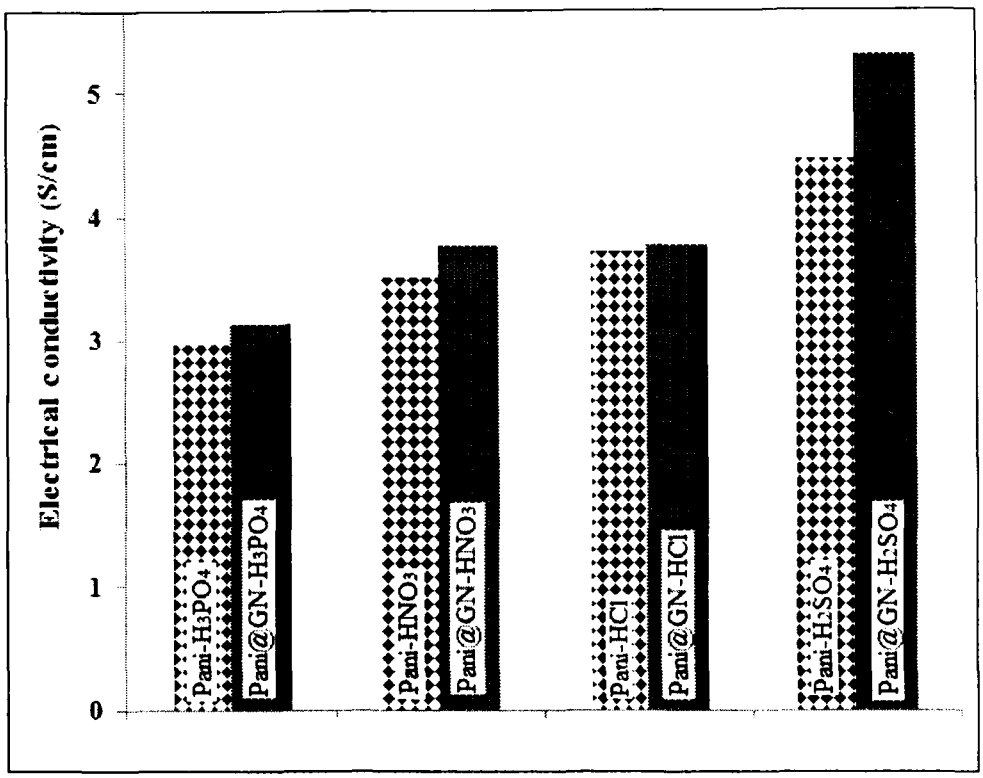


Figure 3.10. The comparison of Initial conductivity of Pani and Pani@GN nanocomposite doped with different acids.

DC Electrical Conductivity Retention under Isothermal Ageing: The electrical conductivity of Pani and Pani@GN nanocomposite was examined under isothermal aging conditions. Heating was done at temperatures 50, 70, 90, 110 and 130 ^{0}C in ambient atmosphere and electrical conductivity was recorded as given in **Table. 3.1** and **Table. 3.2**. The change in the relative electrical conductivity during each experiment was divided by the duration of the experiment (40 minutes) to obtain the relative electrical conductivity loss/gain per minute of heating according to the following equation:

$$\text{CHANGE IN RELATIVE ELECTRICAL CONDUCTIVITY/MIN} = \frac{\text{FINAL RELATIVE ELECTRICAL CONDUCTIVITY} - \text{INITIAL RELATIVE ELECTRICAL CONDUCTIVITY}}{\text{DURATION OF EXPERIMENT (40 MIN)}}$$

From the **Figure 3.11**, it may be observed that the change in relative EC increases with increase in temperature in all the cases of differently doped Pani. However, the higher change was observed in H_2SO_4, HNO_3 and HCl doped Pani while minimum in case of H_3PO_4 doped Pani.

In the case of Pani@GN nanocomposite at shown in **Figure 3.12**, maximum decrease in electrical conductivity was observed in HNO_3 doped Pani@GN. HNO_3 is an oxidizing agent and may degrade the Pani backbone leading to a great loss in electrical conductivity.

In case of H_3PO_4 doped Pani and Pani@GN nanocomposite, positive change or gain in electrical conductivity at 50, 70 and 90°C and negative change or loss in electrical conductivity at 110 and 130°C suggest that both the materials are good semiconductors and stable at lower temperatures but undergo degradation at elevated temperatures as evident from **Figure 1.13**.

Negative change in electrical conductivity was observed at much lower temperature and a very high loss was observed at130°C in the case of HNO_3 doped Pani and Pani@GN nanocomposite due to its strong oxidizing effect as evident from **Figure 3.14**.

The negative change in electrical conductivity uniformly increases with increase in isothermal ageing temperature being highest at 130°C in case of HCl doped Pani and Pani@GN nanocomposite as evident from **Figure 3.15**. This may be attributed to the volatile nature of HCl in comparison to other acids.

Table 3.1. DC electrical conductivity under isothermal ageing conditions of Pani at 50, 70, 90, 110 and 130°C.

Temp. (°C)	Time (min)	DC Electrical Conductivity (S/cm)			
		Pani:H_2SO_4	Pani:HNO_3	Pani: H_3PO_4	Pani:HCl
50	00	7.725336	3.787311	3.112754	3.79462
	10	7.857393	3.810334	3.126871	3.776693
	20	5.19387	3.821951	3.137543	3.735514
	30	4.987242	3.833639	3.148288	3.700926
	40	4.907375	3.833639	3.148288	3.650228
70	00	5.06045	4.220875	3.330797	3.997
	10	11.07608	4.206711	3.443071	4.010368
	20	9.677	4.185643	3.477806	3.990349
	30	8.408369	4.178667	3.495437	3.977114
	40	8.183813	4.164784	3.50432	3.963967
90	00	8.672783	4.533816	3.66742	4.321081
	10	8.25732	4.575182	3.721862	4.35245
	20	7.703757	4.550272	3.752245	4.297849
	30	6.792968	4.501257	3.752245	4.22963
	40	6.183733	4.44539	3.731935	4.163542
110	00	6.743142	4.76654	3.835744	4.376277
	10	5.376111	4.668901	3.793535	4.290161
	20	5.223381	4.533816	3.726892	4.113551
	30	5.184107	4.375567	3.66255	3.950906
	40	5.135838	4.263946	3.600392	3.843269
130	00	5.28342	4.49319	3.638391	4.120619
	10	5.164691	3.979683	3.456015	3.650228
	20	4.996277	3.531268	3.298923	3.326214
	30	4.881319	3.076319	3.184642	3.094452
	40	4.788099	2.746112	3.078013	2.924634

Table 3.2. DC electrical conductivity under isothermal ageing conditions of Pani@GN nanocomposite at 50, 70, 90, 110 and 130°C.

Temp. (°C)	Time (min)	DC Electrical Conductivity (S/cm)			
		Pani@GN:H_2SO_4	Pani@GN:HNO_3	Pani@GN: H_3PO_4	Pani@GN:HCl
50	00	6.822374	4.642661	4.234421	4.120619
	10	6.666533	4.7448	4.255246	3.983721
	20	6.649656	4.7448	4.269243	3.997
	30	6.632864	4.716501	4.283333	3.983721
	40	6.566535	4.716501	4.304643	4.003673
70	00	7.079822	5.058422	4.437094	4.297849
	10	6.894	5.202632	4.702355	4.252128
	20	6.683496	5.225551	4.762752	4.192657
	30	6.469493	5.202632	4.806852	4.134828
	40	6.024344	5.202632	4.824721	4.106507
90	00	6.010558	5.569014	4.953626	4.424723
	10	6.180268	5.608511	5.30818	4.321081
	20	6.224204	5.569014	5.275813	4.26726
	30	6.238988	5.478984	5.275813	4.2
	40	6.194844	5.428833	5.265112	4.156326
110	00	6.566535	5.648571	5.38527	4.457621
	10	6.406376	5.569014	5.38527	4.368306
	20	6.180268	5.343243	5.329979	4.2825
	30	6.224204	5.036943	5.254453	4.214763
	40	6.038193	4.763855	5.181038	4.149135
130	00	6.469493	4.651765	5.275813	4.207368
	10	6.136949	3.509467	5.040194	3.983721
	20	5.915797	2.584314	4.860861	3.747188
	30	5.624441	1.750849	4.719455	3.516422
	40	5.660806	1.289348	4.618683	3.1976

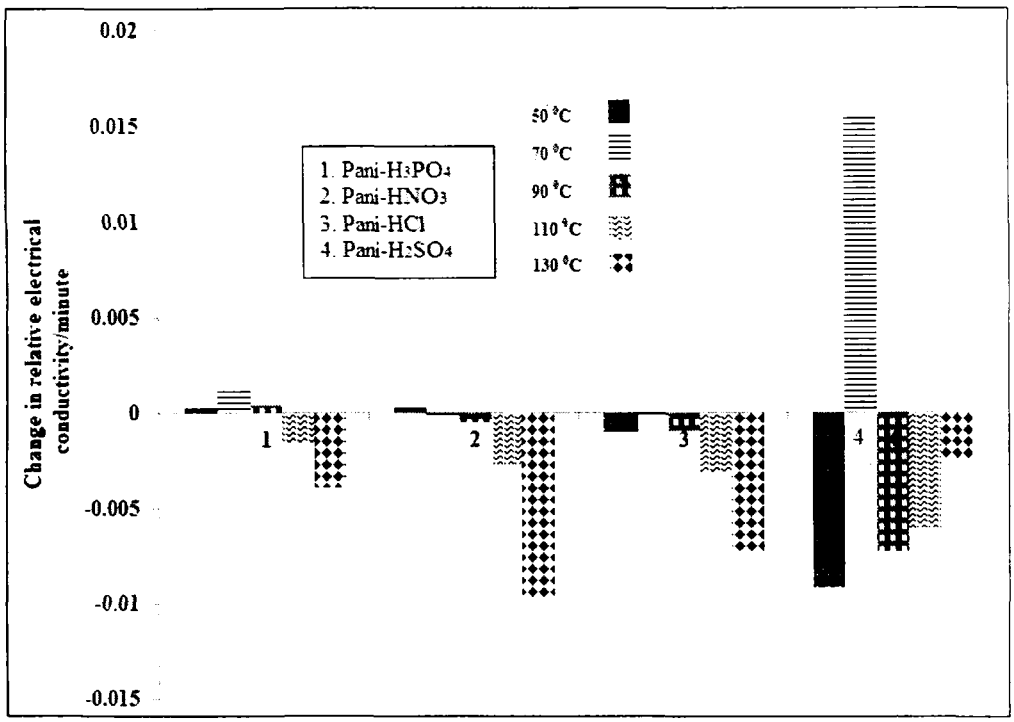


Figure 3.11. Change relative electrical conductivity /minute of Pani doped with different acids under isothermal ageing condition.

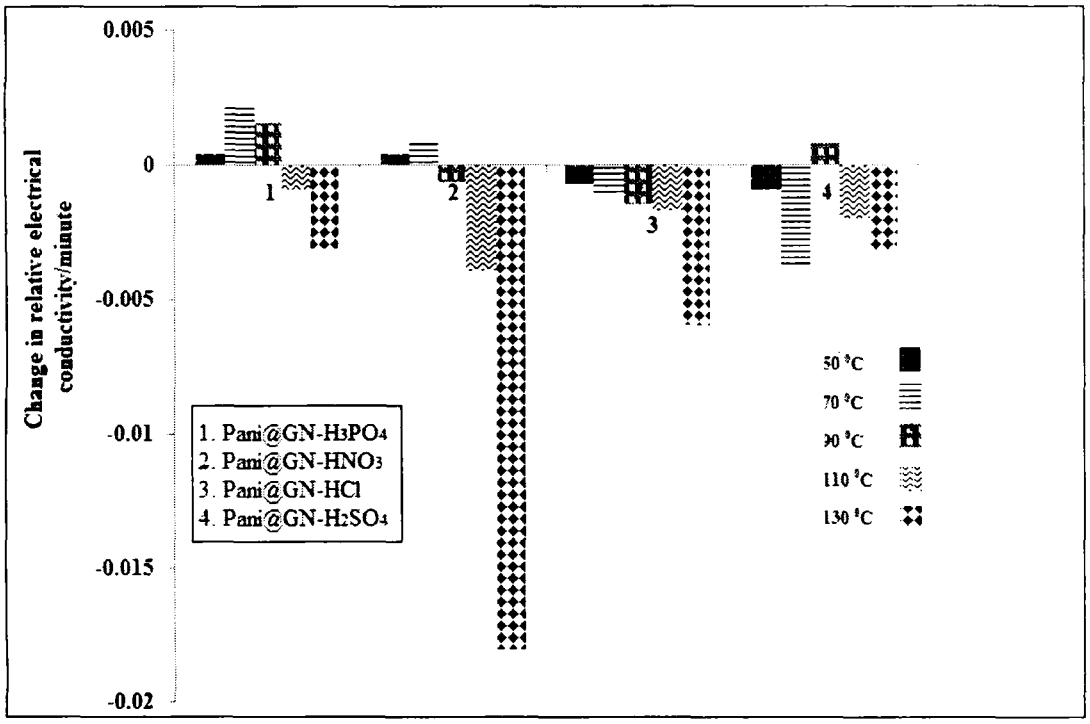


Figure 3.12. Change relative electrical conductivity /minute of Pani@GN nanocomposite doped with different acids under isothermal ageing condition.

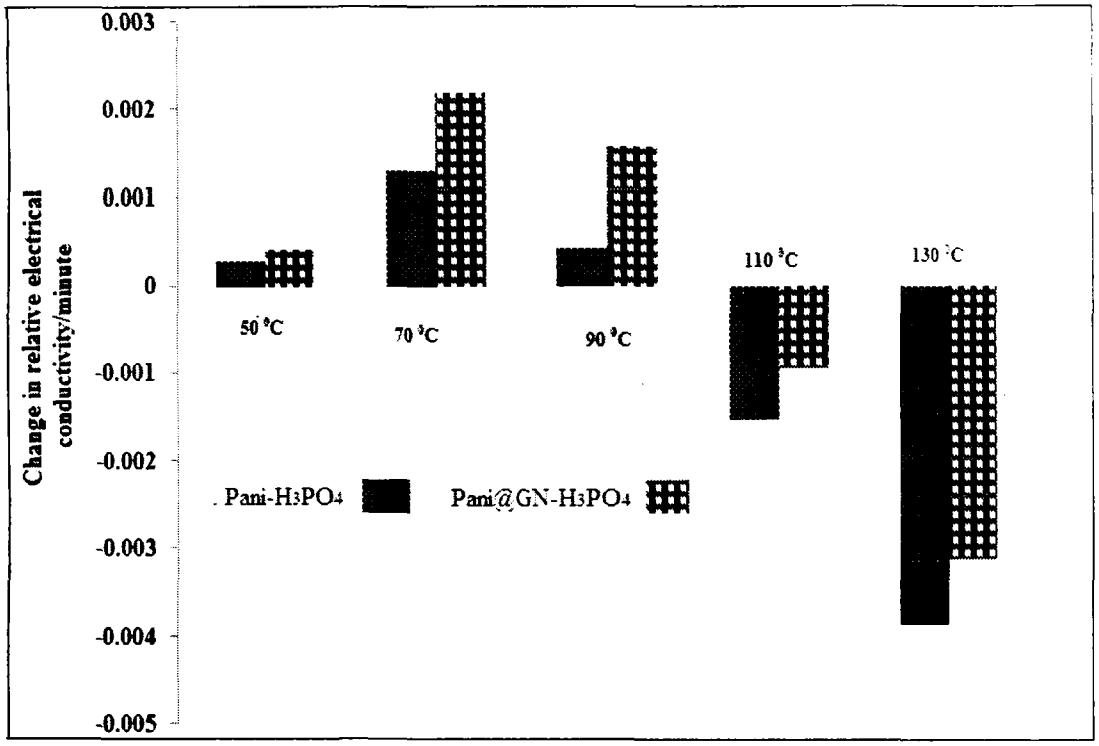


Figure 3.13. Change relative electrical conductivity /minute of Pani and Pani@GN nanocomposite doped with H_3PO_4 under isothermal ageing condition.

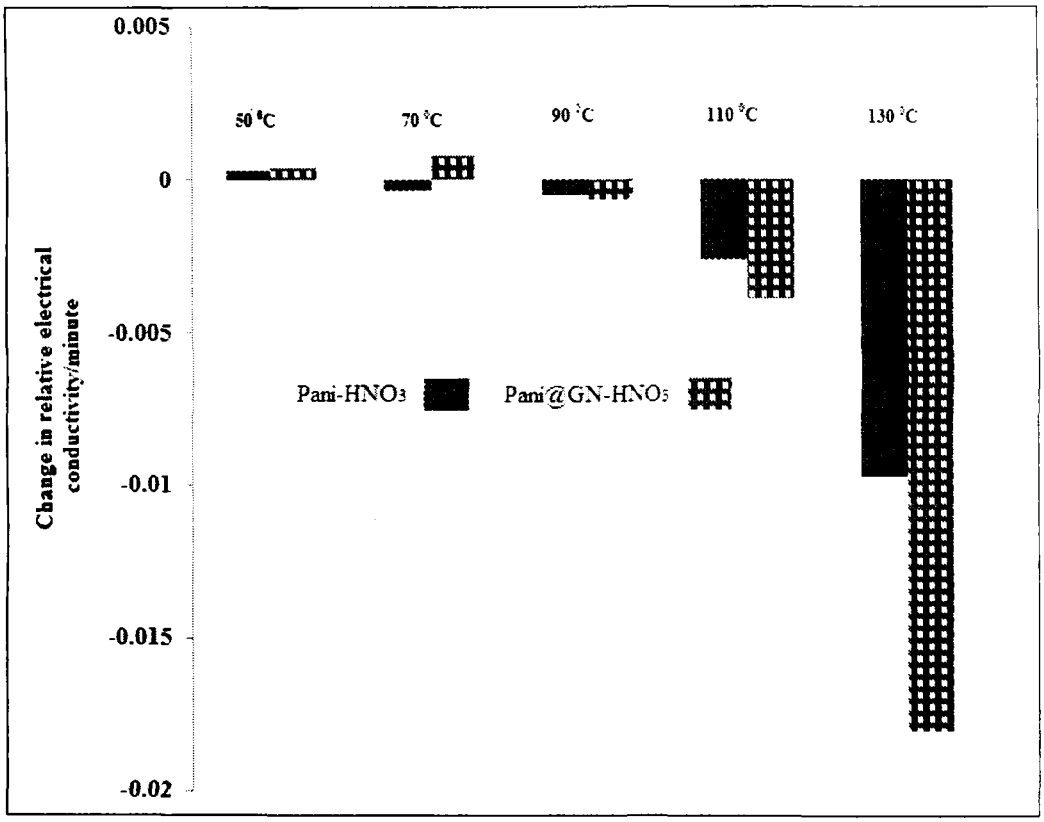


Figure 3.14. Change relative electrical conductivity /minute of Pani and Pani@GN nanocomposite doped with HNO_3 under isothermal ageing condition.

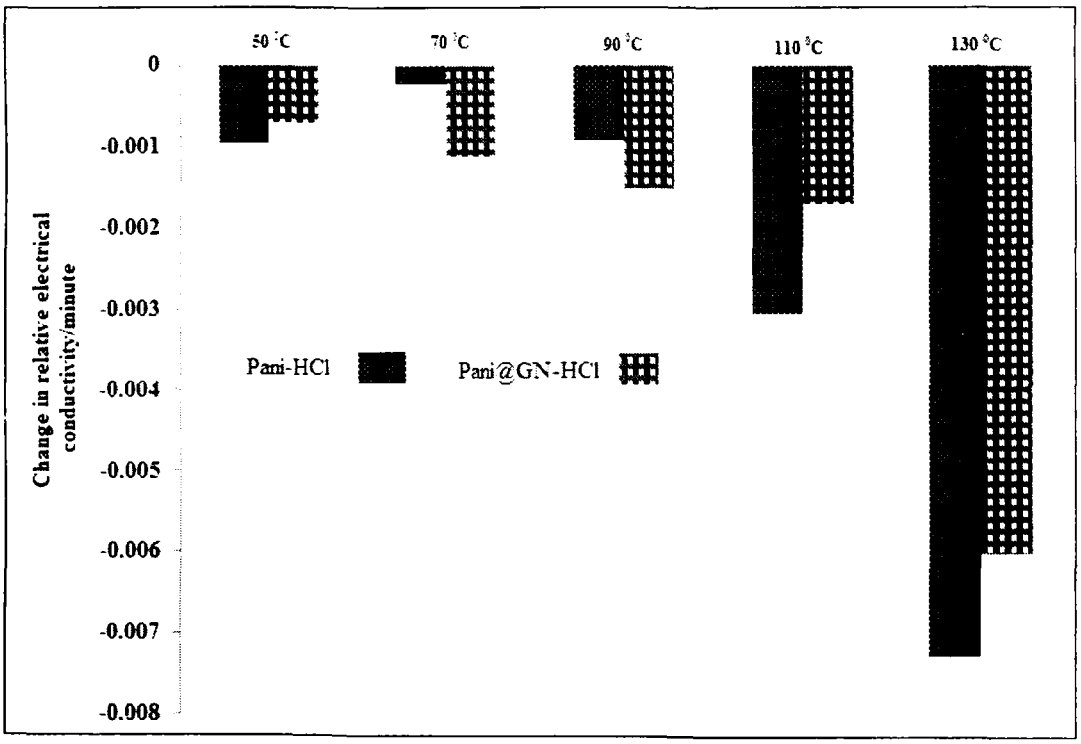


Figure 3.15. Change relative electrical conductivity/minute of Pani and Pani@GN nanocomposite doped with HCl under isothermal ageing condition.

In case of H_2SO_4 doped Pani and Pani@GN nanocomposite the negative change in the electrical conductivity decreases from lower to higher temperature as shown **Figure 3.16**. There may be some instrumental problem in recording the data as not very regular loss/gain pattern of electrical conductivity is observed in this case.

Under cyclic ageing conditions: The stability in terms of DC electrical conductivity retention of Pani and Pani@GN nanocomposite was also studied by cyclic ageing technique as given in (**Table 3.3** and **Table. 3.4**).

In case of HCl doped Pani and Pani@GN nanocomposite a uniform increase in the positive change in electrical conductivity was observed from cycle 1^{st} to 5^{th} while different trends were observed in other cases as evident from **Figure 3.17** and **Figure 3.18** respectively.

Pani and Pani@GN nanocomposite doped with H_3PO_4 showed large positive change in electrical conductivity in 1^{st} and 2^{nd} cycle and comparatively lower positive change in cycle 3^{rd}, 4^{th} and 5^{th} cycle as shown in **Figure 3.19**. The change is greater in case of Pani@GN nanocomposite compared to pure Pani in all the cycles.

No very regular trends in changes in electrical conductivity of HNO_3 and H_2SO_4 doped Pani and Pani@GN nanocomposite were observed as evident respectively from **Figure 3.20** and **Figure 3.21**.

In case of HCl doped Pani and Pani@GN, the positive change in electrical conductivity increases with increase in cycle number as evident from **Figure 3.22**. This supports the stability of semiconductor nature of both these materials during cyclic ageing [7].

Form **Figure 3.23**, it may be observed that the positive change in electrical conductivity seems to decrease with increase in cycle number in case Pani doped with H_2SO_4 and HCl while an increase followed by a decrease in case of Pani doped with H_3PO_4 and HNO_3.

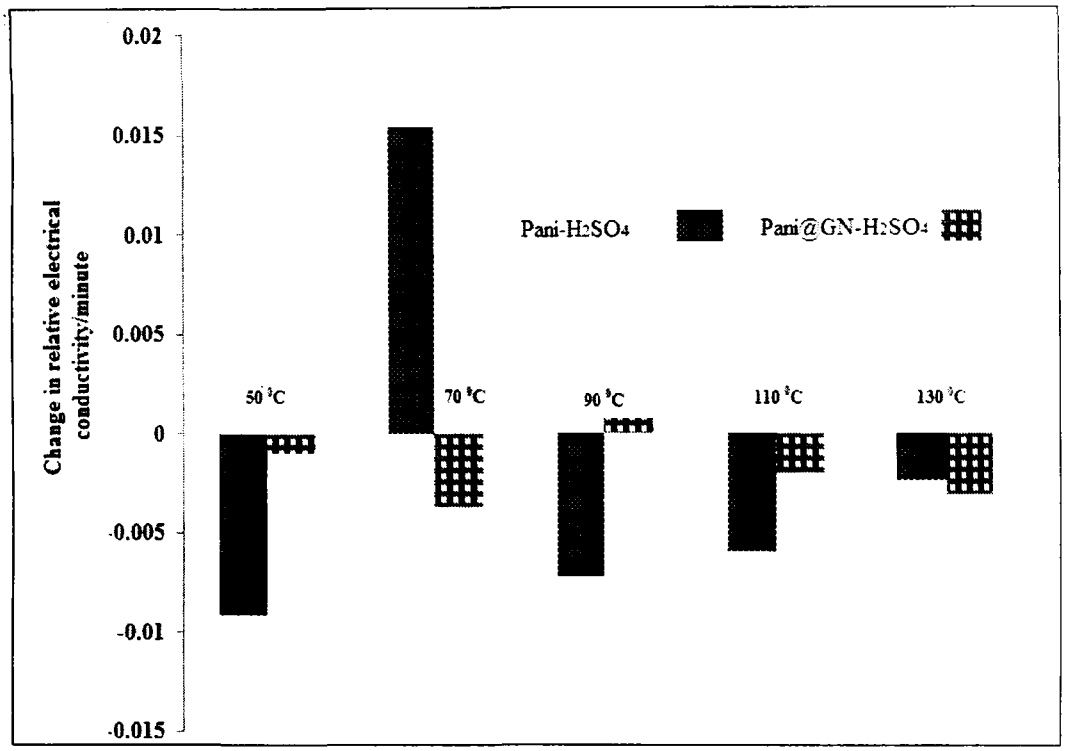


Figure 3.16. Change relative electrical conductivity /minute of Pani and Pani@GN nanocomposite doped with H_2SO_4 under isothermal ageing condition.

Table 3.3. Electrical conductivity under cyclic ageing of Pani from 40-150°C.

Temp. (°C)	Sample I.D	DC Electrical Conductivity- σ (S/cm)				
		Cycle-1	Cycle-2	Cycle-3	Cycle-4	Cycle-5
40	Pani-H_2SO_4	4.463413	3.658356	4.19938	3.487205	3.233796
50		4.587015	3.717656	4.253295	3.532654	3.258536
60		4.040054	3.872156	4.217199	3.579304	3.290905
70		3.592241	3.959575	4.205303	3.713026	3.438939
80		4.034587	4.078741	4.193474	3.837272	3.600918
90		4.308613	4.181711	4.290014	3.902565	3.75039
100		4.510681	4.211243	4.42368	4.089931	3.862124
110		4.615418	4.253295	4.545061	4.371789	3.991379
120		4.503867	4.290014	4.680628	4.503867	4.152591
130		4.158382	4.283851	4.83235	4.687987	4.296196
140		3.391991	4.290014	5.002617	4.840195	4.456741
150		3.320223	4.463413	5.053492	4.952757	4.572945
40	Pani-HNO_3	3.502152	4.1364	3.061322	2.52559	2.163603
50		3.709907	4.236474	3.291496	2.669323	2.295991
60		3.955744	4.528645	3.511516	2.830403	2.441091
70		4.277873	4.724126	3.632938	2.998418	2.590349
80		4.640661	4.900399	3.874062	3.172239	2.736056
90		5.022207	5.012622	4.091299	3.350273	2.886389
100		5.415699	5.1705	4.291853	3.525656	3.033042
110		5.811093	5.274325	4.474641	3.678731	3.164595
120		6.151321	5.360437	4.62432	3.812212	3.287377
130		6.298835	5.393458	4.690382	3.920319	3.397948
140		6.375277	5.360437	4.707194	3.979718	3.46519
150		6.406376	5.221897	4.648874	3.932057	3.433482
40	Pani-H_3PO_4	2.969602	3.522278	3.206119	2.997683	2.865582
50		3.123202	3.670101	3.345699	3.127053	2.994144
60		3.255507	3.819337	3.483571	3.268093	3.115528
70		3.385901	3.956381	3.612593	3.385901	3.243018
80		3.517393	4.0838	3.740472	3.507663	3.363448
90		3.680755	4.198742	3.854164	3.617746	3.469275
100		3.950218	4.305671	3.950218	3.718534	3.571887
110		4.276627	4.387612	4.03828	3.796467	3.659509
120		4.57769	4.464859	4.110276	3.871817	3.729471
130		4.839771	4.512527	4.164269	3.931845	3.785134
140		4.972627	4.52057	4.191802	3.974984	3.830876
150		4.92435	4.433636	4.123642	3.974984	3.842485
40	Pani-HCl	3.701629	3.042117	2.49441	2.261723	2.051241
50		3.923248	3.215606	2.652699	2.405324	2.182329
60		4.116413	3.400515	2.802968	2.57385	2.32684
70		4.345102	3.586638	2.971283	2.712044	2.466497
80		4.531901	3.730103	3.140631	2.859159	2.601467
90		4.763393	3.904395	3.298731	3.023151	2.748942
100		4.999107	4.081763	3.458726	3.165231	2.893278
110		5.282281	4.268604	3.635033	3.307731	3.038305
120		5.535541	4.376475	3.764856	3.4197	3.173517
130		5.612424	4.50663	3.891761	3.560304	3.303225
140		5.305396	4.540388	4.000936	3.684752	3.453799
150		4.618223	4.392332	4.02752	3.776584	3.539514

Table 3.4. Electrical conductivity under cyclic ageing of Pani@GN from 40-150°C.

40	Pani@GN-H_2SO_4	5.306291	7.398913	3.242733	7.29615	9.248641
50		5.612423	9.586182	3.411187	7.569493	10.85378
60		5.956041	10.10236	3.544688	7.569493	11.88513
70		6.298835	10.4646	3.573624	6.344478	13.06773
80		6.666533	9.448252	3.447	5.284938	14.43195
90		6.752221	7.176541	3.329042	4.444355	15.45067
100		7.098957	4.8641	3.324828	3.967695	15.72823
110		7.504611	4.444355	3.502152	3.583375	8.555746
120		8.00797	4.250184	3.991815	3.384812	3.262875
130		8.2339	4.974648	4.459447	3.411187	2.475602
140		8.555746	6.298835	5.529714	3.89128	2.555072
150		8.995253	7.725335	7.29615	5.253228	0.964957
40	Pani@GN-HNO_3	3.759746	2.609901	1.427437	2.791059	0.593694
50		4.076289	2.791059	1.50533	3.741956	0.630957
60		4.393333	3.018321	1.629396	5.595283	0.669791
70		4.735329	3.214634	1.732944	9.722951	0.738605
80		4.973585	3.336709	1.853438	2.24286	0.805842
90		5.283742	3.488824	1.968797	1.217864	0.857701
100		5.608511	3.863844	2.073776	1.293566	0.916692
110		5.901493	4.062329	2.202786	1.365017	0.980331
120		6.517582	4.28231	2.344269	1.40545	0.986855
130		7.277301	4.476226	2.38672	1.45546	1.020826
140		7.881728	4.251613	2.391532	1.466255	1.04511
150		7.961074	3.583686	1.941408	1.365017	1.003553
40	Pani@GN- H_3PO_4	3.134741	4.37572016	2.876905	2.510161	2.262349
50		3.226044	4.94558139	3.003684	2.621558	2.369216
60		3.306294	5.26386138	3.138442	2.748976	2.475102
70		3.408026	5.43887468	3.273719	2.864504	2.595957
80		3.48853	5.49509043	3.386318	2.963501	2.687826
90		3.544347	5.62592592	3.479398	3.066044	2.786436
100		3.797514	5.90722222	3.582561	3.160832	2.876905
110		4.153531	6.21812865	3.661515	3.24178	2.963501
120		4.445251	6.68742138	3.717846	3.314539	3.038011
130		4.922704	7.56797153	3.770582	3.390638	3.112717
140		5.337871	8.11679389	3.808395	3.443342	3.179737
150		6.0415	8.78760330	3.813859	3.452286	3.210459
40	Pani@GN-HCl	4.09249146	3.435816619	2.679553073	2.339707317	2.107381371
50		4.30556553	3.678220859	2.821411765	2.467283951	2.188138686
60		4.576717557	3.874313409	2.931784841	2.578709677	2.305961538
70		4.777290837	4.010367893	3.028030303	2.722133939	2.393413174
80		4.934567901	4.214762742	3.155526316	2.855	2.498125
90		5.080932203	4.344565217	3.280711354	3.01281407	2.641189427
100		5.236244541	4.424723247	3.435816619	3.155526316	2.737671233
110		5.551388889	4.594252874	3.644680851	3.276229508	2.88939759
120		5.737320574	4.693150685	3.7471875	3.475652174	3.016603774
130		5.863569682	4.7964	3.861835749	3.628139183	3.163852243
140		5.936138614	4.894285714	3.990349418	3.700925926	3.321606648
150		5.980548628	4.944742268	3.937931034	3.753051643	3.377746479

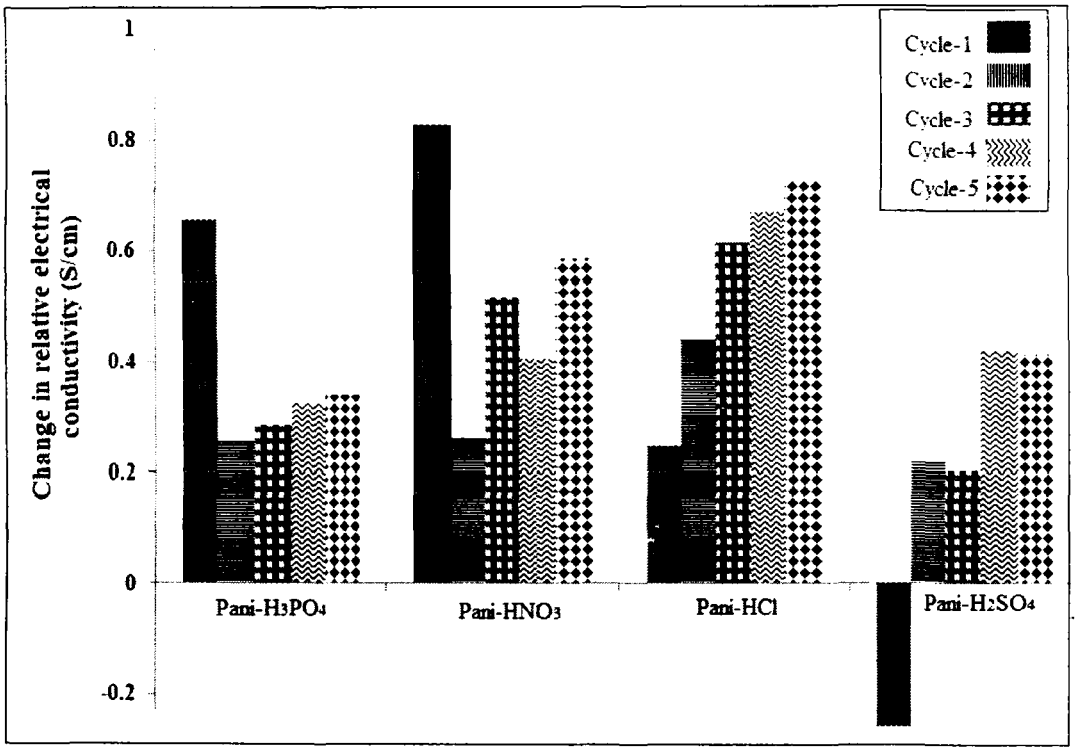


Figure 3.17. DC electrical conductivity retention under cyclic ageing conditions of and Pani@GN nanocomposite doped with different acids.

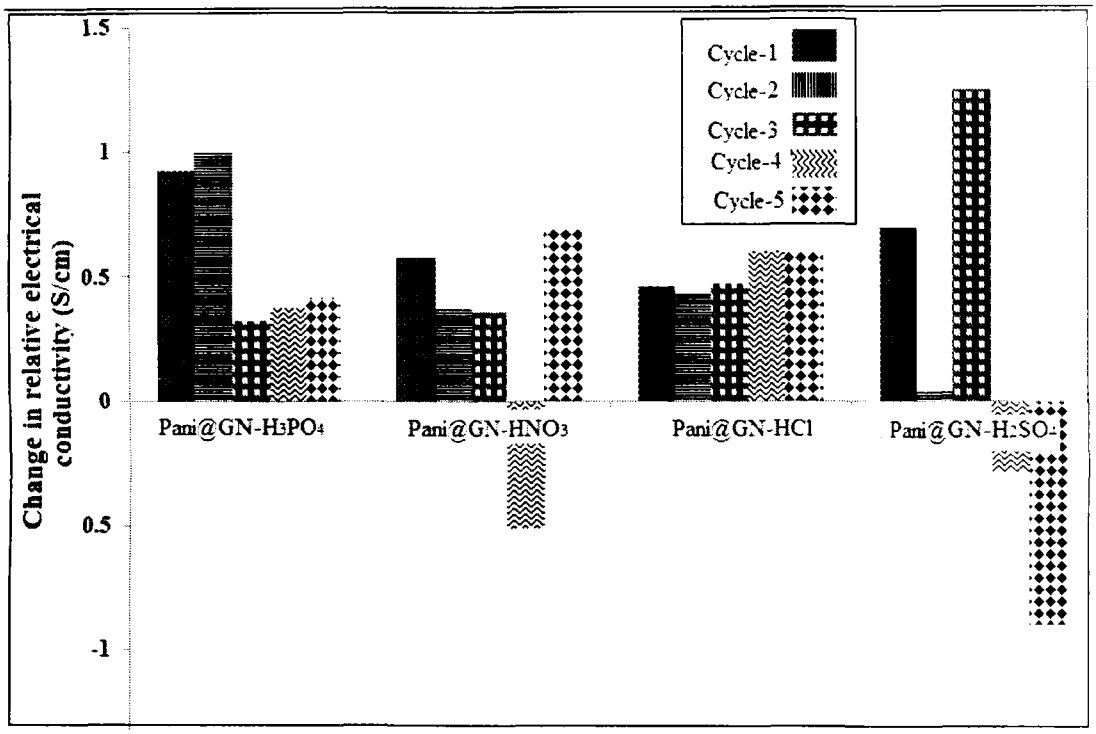


Figure 3.18. DC electrical conductivity retention under cyclic ageing conditions of Pani doped with different acids.

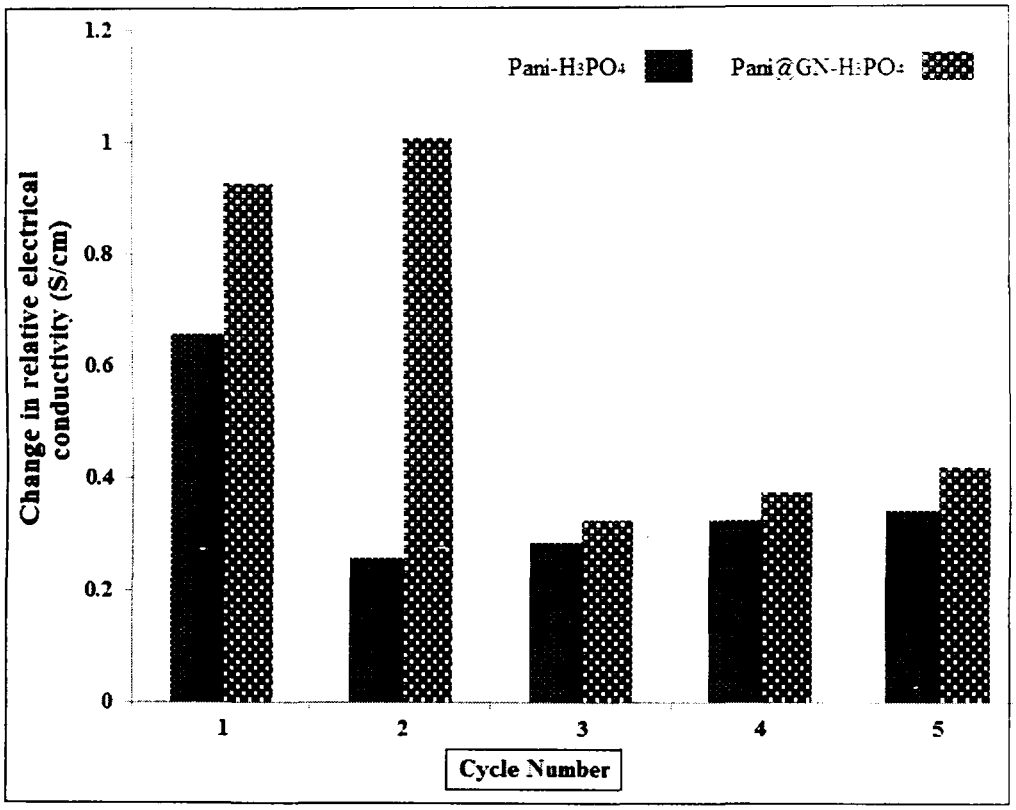


Figure 3.19. DC electrical conductivity retention under cyclic ageing conditions of Pani and Pani@GN nanocomposite doped with H_3PO_4.

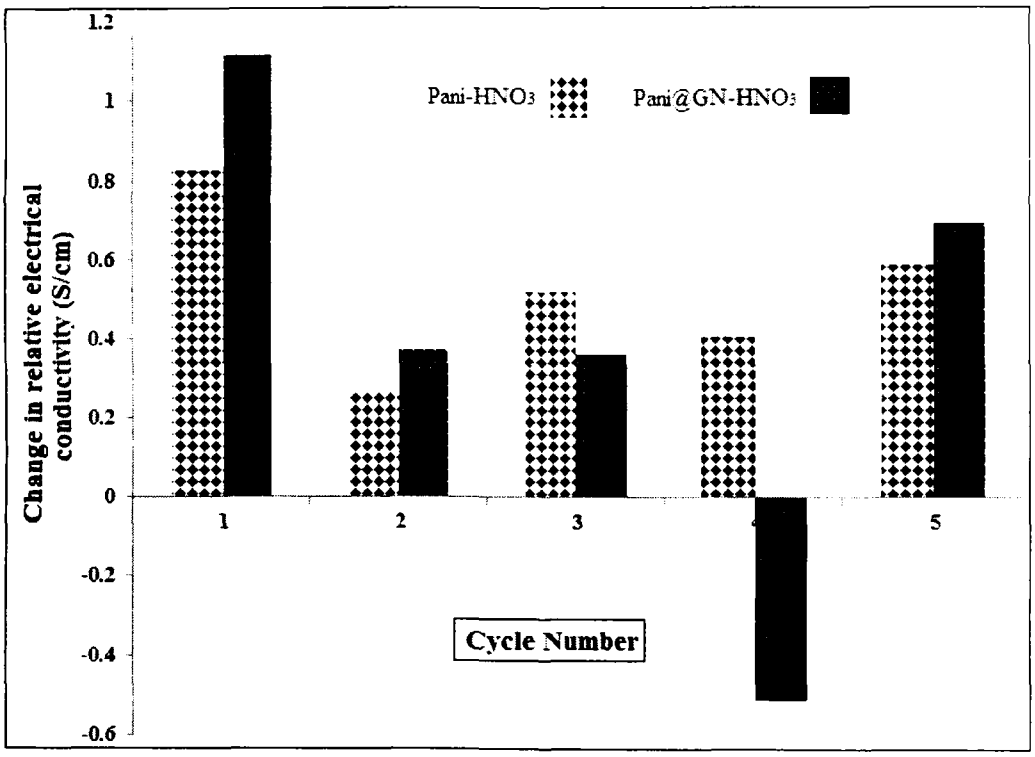


Figure 3.20. DC electrical conductivity retention under cyclic ageing conditions of Pani and Pani@GNnanocomposite doped with HNO_3.

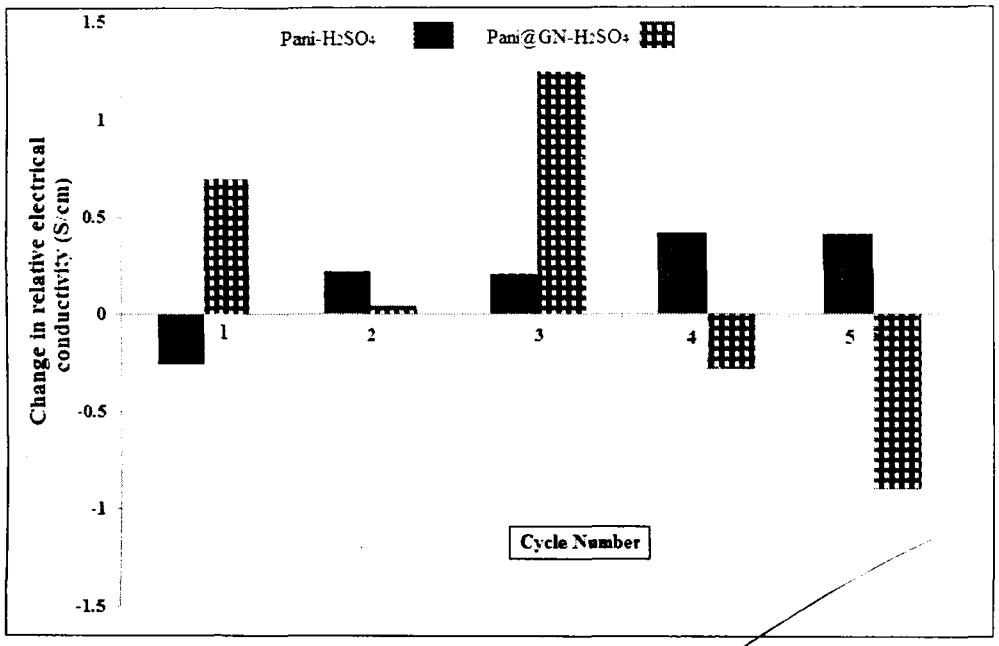


Figure 3.21. DC electrical conductivity retention under cyclic ageing conditions of Pani andPani@GN nanocomposite doped with H_2SO_4.

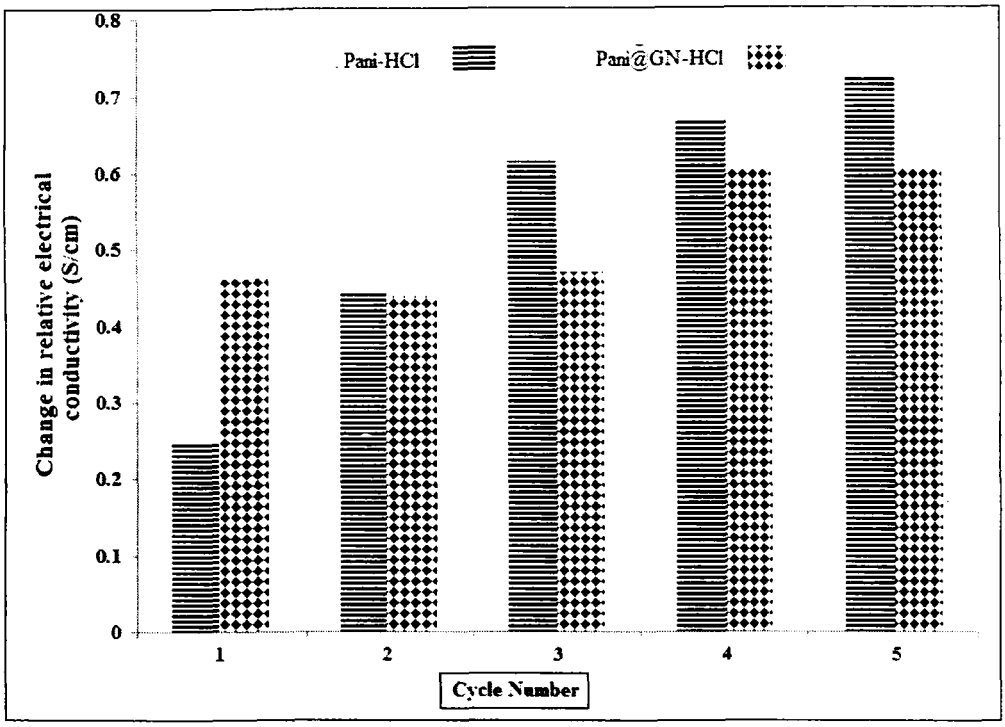


Figure 3.22. DC electrical conductivity retention under cyclic ageing conditions of Pani and Pani@GN nanocomposite doped with HCl.

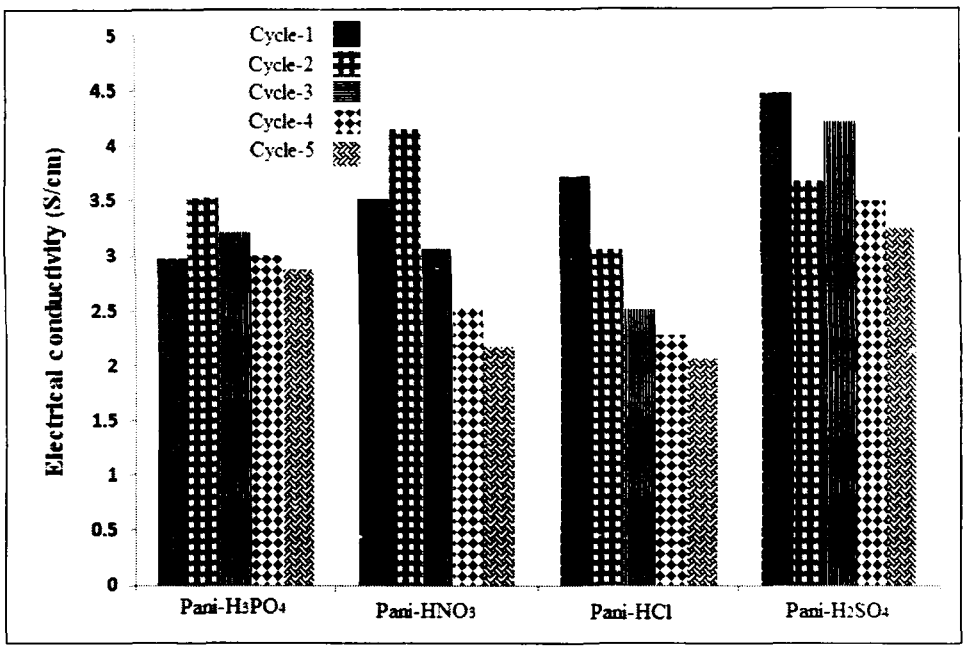


Figure 3.23. Electrical conductivity at the beginning of each cycle of Pani doped with different acids.

The positive change in electrical conductivity seems to decrease with increase in cycle number in case of H_3PO_4, HNO_3 and HCl doped Pani@GN nanocomposite while no trends was observed in case of Pani@GN nanocomposite doped with H_2SO_4 as shown in **Figure 3.24** [7].

The positive change in electrical conductivity and its difference in Pani and Pani@GN nanocomposite doped with H_3PO_4 and HNO_3 are maximal in second cycle as shown in **Figure 3.25** and **Figure 3.26** respectively.

The positive change in electrical conductivity and its difference in Pani and Pani@GN nanocomposite doped with HCl are maximal in first cycle as shown in **Figure 3.27**.

The positive change in electrical conductivity and its difference in Pani and Pani@GN nanocomposite doped with H_2SO_4 are maximal in fifth cycle as shown in **Figure 3.28**.

Hatchett *et al* [1] explained that the anions which can form hydrogen bond will interact with the amine groups of Pani more strongly than those that do not. Since Cl^- also have ability to form hydrogen bond which will result in less delocalized charge on Pani backbone and subsequently a decrease in DC electrical conductivity interpreted that anionic radical such as HSO_4^-, PO_4^{3-} and NO_3^- induce cross linking in the Pani chains in comparison to monovalent Cl^- resulting in decrease in electrical conductivity.

The loss or gain in electrical conductivity may be attributed to several factors as explained here. The increase in electrical conductivity with rise in temperature may be attributed to, for example, (1) semiconductor effect i.e. semiconductors show enhanced electrical conductivity with increase in temperature due to increase in number of charge carriers and (2) annealing effect during heating/ageing (isothermal as well as cyclic) i.e. annealing causes increase in crystallinity leading to increased mobility of charge carriers. The decrease in electrical conductivity may be attributed to, for example, (1) volatilization of dopant i.e. the extent of doping decreases, (2) removal of trapped moisture in the nanocomposites and (3) degradation of polymer due to the reaction of polymer with dopant or atmospheric oxygen etc [9].

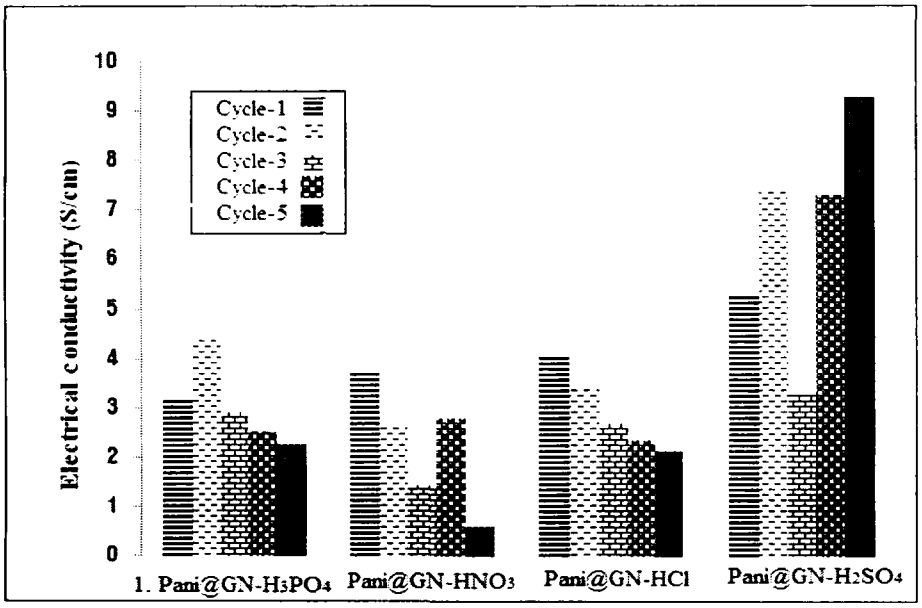


Figure 3.24. Electrical conductivity at the beginning of each cycle of Pani@GN nanocomposite doped with different acids.

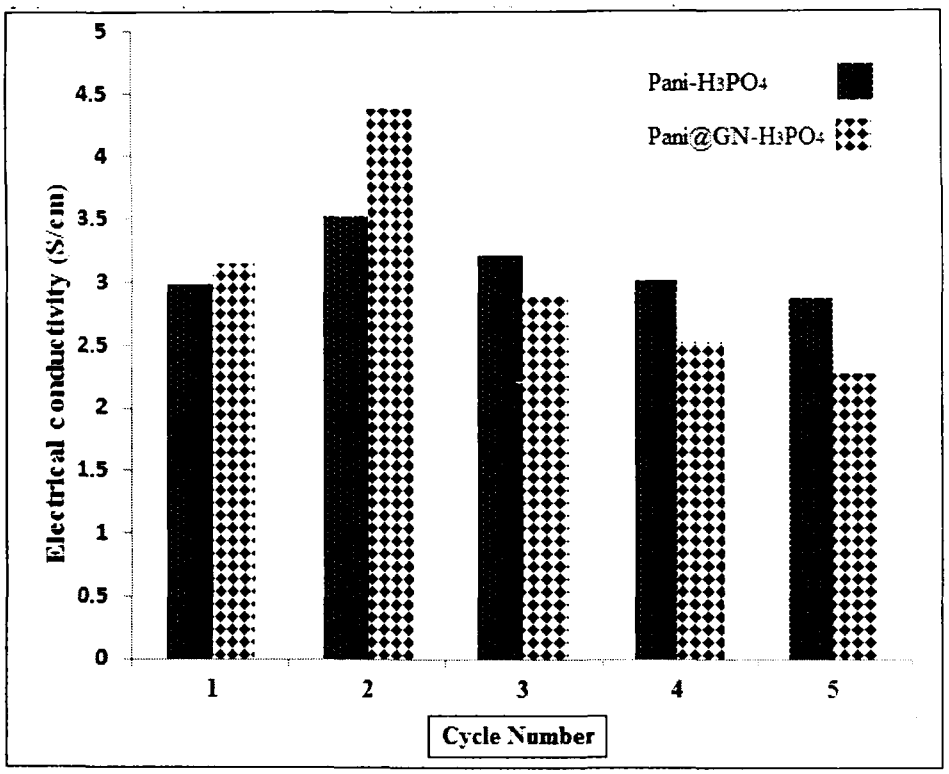


Figure 3.25. Electrical conductivity at the beginning of each cycle of Pani and Pani@GN nanocomposite doped with H_3PO_4.

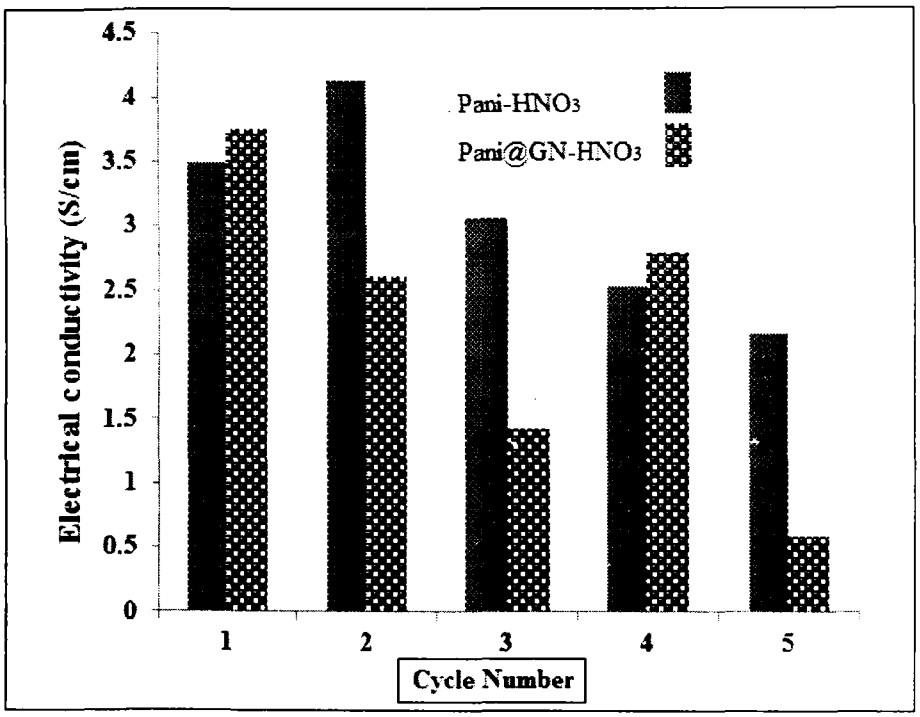


Figure 3.26. Electrical conductivity at the beginning of each cycle of Pani and Pani@GN nanocomposite doped with HNO_3.

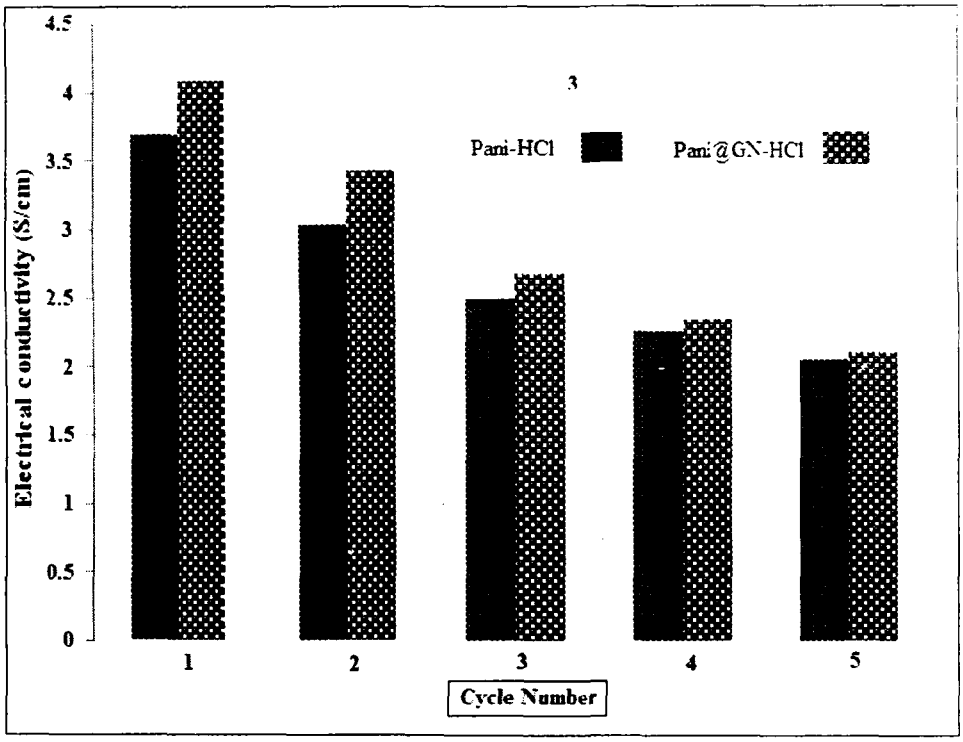


Figure 3.27. Electrical conductivity at the beginning of each cycle of Pani and Pani@GN nanocomposite doped with HCl.

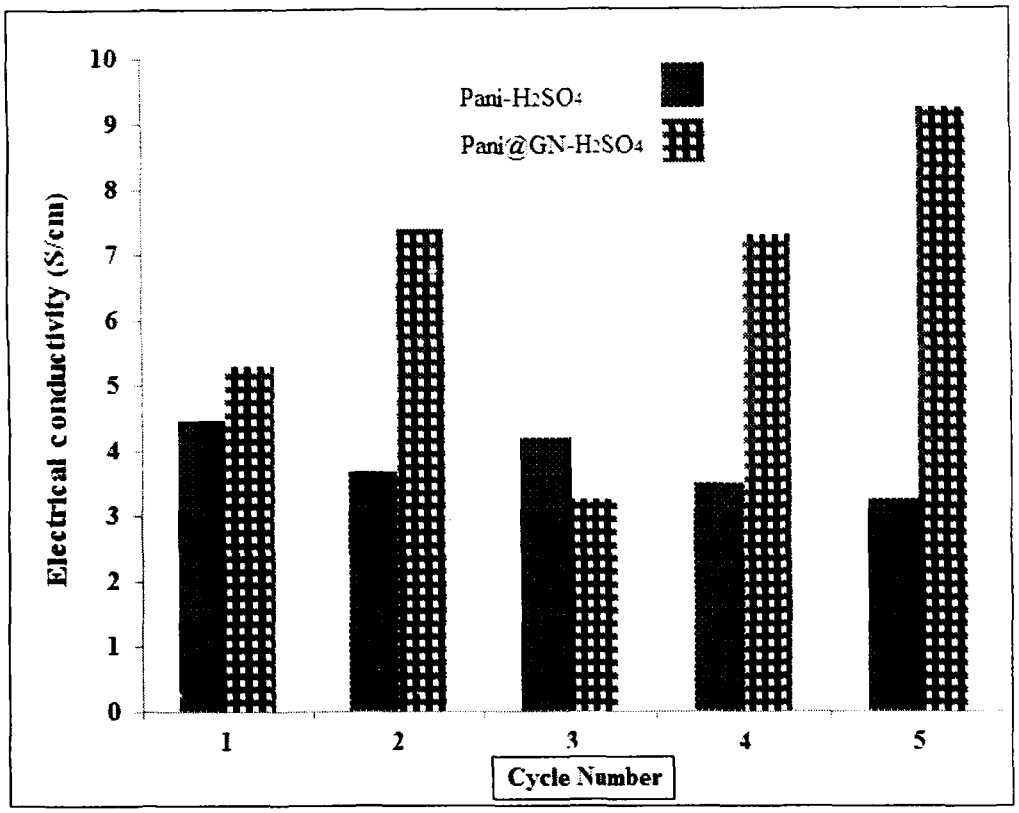


Figure 3.28. Electrical conductivity at the beginning of each cycle of Pani and Pani@GN nanocomposite doped with H_2SO_4.

Chapter –4

Conclusions

CONCLUSIONS

The objective of this study was to prepare nanocomposite of polyaniline (Pani) with Graphene (GN) by *in-situ* oxidative polymerization of aniline in the presence of GN nanoplatelets. Pani@GN nanocomposites were doped with different acids and the stability of these nanocomposites in terms of DC electrical conductivity retention was studied by isothermal and cyclic ageing techniques under ambient atmosphere. Pani@GN nanocomposites were observed to be thermally more stable than Pani and the stability was highly dependent on the type of acid used in doping of the Pani and Pani@GN nanocomposites.

The samples were characterized by fourier transform infrared spectroscopy, x-ray diffraction , scanning electron microscopy, diffused rays spectroscopy and transmission electron microscopy. Pani@GN nanocomposites have shown enhanced electrochemical properties, thermal stability, electric properties, optical properties, etc. The enhancement due to the large surface area and unique properties of graphene and the good electro catalytic activity of Pani. They may find applications in electronic, lithium ion batteries, sensing, fuel cells, solar cells, photocatalysis, supercapacitors, anticorrosion coatings, electrical and optical applications etc.

Another set of materials, Pani and Pani@GN nanocomposites, by *in situ* oxidative polymerization method doped with dodecylbenzenesulphonic acid (DBSA) was also successfully prepared. The work on characterization is in progress.

References

REFERENCES

Chapter 1

[1] Hornyak G L, Harry F, Tibbals, Dutta J. Introduction to Nanoscience and Nanotechnology. CRC Press, 2009.

[2] Sharma P, Bhargava M. Applications and characteristics of nanomaterials in industrial environment, Int. Journal of Civil, Structural, Environmental and Infrastructure Engineering Research and Development (IJCSEIERD) 2013;3:63-72.

[3] www.gitam/edu/eresource/nano/nanotechnology/nano_materials.htm, History of Nanomaterials.

[4] Paciotti GF, Kingston DGI, Tamarkin L, Colloidal gold nanoparticles: a nove nanoparticle platform for developing multifunctional tumor-targeted drug delivery vectors. Drug Dev Res 2006;67:47–54.

[5] Moon S, Lin A, Kim BH, Watekar PR, Han WT, Linear and nonlinear optical properties of the optical fiber doped with silicon nano-particles. J Non-Crystall Solids 2008;354:602 - 606.

[6] Klement JW, Willens RH, Duwez P, Non-crystalline structure in solidified gold-silicon alloy. Nature 1960;187:869-870.

[7] Granqvist CG, Buhrman RA, Ultrafine metal part. Journal of Applied Physics 1976;47:2200-2219.

[8] Jose-Yacaman M, Rendon L, Arenas J, Serra Puche MC. Maya blue paint: an ancient nanostructured material. Science 1996;273:223-5.

[9] Dutta J, Hofmann H. Self-organization of colloidal nanoparticles. Encyclopedia of nanoscience and nanotechnology.Edited by H. S. Nalwa. X:1–23)

[10] Cole, Bergeson, Hutton. Use of nanoscale materials in commercial sunscreen Products. Nanotech Law & Business 74(9) (Spring-Summer 2012)

[11] Mayer P. Microencapsulation technologies. PCHI, Proceedings; Shanghai 2008;15.

[12] Raghunathan S. Nanomaterials from NANOMAT-manufacturing, b processing and applications", North Huntingdom, PA 15642-7425.

[13] Chen Y-B. Introduction to nanotechnology - history definition methodology applications and challenges.Nanoscale Engineering Radiation Lab 2012;7-25.

[14] Lane N, Kalil T. The national nanotechnology initiative: present at the creation. 2010 [Online] Available at http://www.issues. org/21.4/lane.html.

[15] Surendiran A, Sandhiya S, Pradhan SC, Adithan C. Novel applications of nanotechnology in medicine. Indian J Med Res 2009;130:689-701.

[16] Filios AA, Ryu YS, Shahrabi K. Optical properties and applications of nanoscale silicon IAJC-IJME International Conference. 2008 ISBN 978-1-60643-379-9.

[17] Crosby AJ, Lee J. Polymer nanocomposites: The 'nano' effect on mechanical properties. Polym Rev 2007;47:217–29.

[18] Noor AK, Venneri SL. Flight-vehicle materials structures and dynamics: Advanced metallic metal-matrix and polymer-matrix composites. American Society of Mechanica Engineers, New York, 1994.

[19] Sanchez C, Julia´n B, Belleville P, Popall M. Applications of hybrid organic–inorganic nanocomposites. J Mater Chem 2005;15:3559–3592.

[20] Allan G, Delerue C, Lannoo M. Quantum confinement in the Si-III (BC-8) phase of porous silicon. Appl. Phys. Lett. 1997;70:2437.

[21] Hoshi Y, Pan W, Kiguchi T, Ooi K, Tayagaki Takeshi, Usami N. Control of dip shape in photonic nanostructures by maskless wet-etching process and its impact on optical Properties. Jpn. J. Appl. Phys. 2013;52:080202.

[22] Sain M, Oksman K. Cellulose Nanocomposites. ACS Symp. Ser. 2006;938:2–8

[23] Siegel RW. Mechanical properties of nanophase materials. Mater Sci Forum.1997;235:851.

[24] Weertman JR, Farkas D, Hemker K, Kung H, Mayo M, Mitra R,VanSwygenhoven H Structure and Mechanical Behavior of Bulk Nanocrystalline Materials. MRS Bull 1999;24:44-53.

[25] Gleiter H. Nanostructured materials: basic concepts and microstructure. Acta Mate 2000;48:1.

[26] Vaben R, Stoever D. Processing and properties of nanophase non-oxide ceramics. Mater Sci Eng 2001;A301:59.

[27] Kuntz JD, Zhan G-D, Mukherjee AK. Nanocrystalline-matrix ceramic composites for improved fracture toughness. MRS Bull 2004;29:22 .

[28] Wang W, Schiff EA. Polyaniline on crystalline silicon heterojunction solar cells. Appl.

Phys. Lett. 2007; 91:133504-3.

[29] Kochuveedu ST, Jang YH, Kim DH. A study on the mechanism for the interaction of light with noble metal-metal oxide semiconductor nanostructures for various photophysical applications. Chem Soc Rev 2013;42:8467-8493.

[30] Schabes ME. Micromagnetic theory of non-uniform magnetization processes in magnetic recording particles. J Magn Magn Mater 1991;95:249-288.

[31] W. P Halperin, Rev. Mod. Phys, 58. (1986) 533, Phys.Lett, 71(3) (1997)410.

[32] Mohammed Cherkaoui, Laurent Capolungo. Atomic and cotinuum modeling of nano crystalline materials. (Springer)

[33] Gustafsson G, Cao Y, Treacy GM, Klavetter F, Colaneri N, Heeger AJ. Flexible light-emitting diodes made from soluble conducting polymers. Nature 1992;357:477- 479.

[34] Jin YD, Chen HZ, Heremans PL, Aleksandrzak K, Geise HJ, Borghs G,Auweraer MV. Efficient blue polymer light-emitting diodes from a novel biphenyl derivative. Synth Met 2002;127:155-158.

[35] Becker S, Ego C, Grimsdale AC, List EJW, Marsitzky D, Pogantsch A, Setayesh S, Leising G, Mullen K. Optimisation of polyfluorenes for light emitting Applications. Synth Met 2002;125:73-80.

[36] Nenashev AV, Baranovskii SD, Wiemer M, Jansson F, Österbacka R, Dvurechenskii AV, Gebhard F. Theory of exciton dissociation at the interface between a conjugated polymer and an electron acceptor. Phys Rev B 2011;84:35210.

[37] Ansari SP, D. Phil Thesis. Aligarh Muslim University. Aligarh. India. 2011.

[38] Chang CM, Liu YL. Electrical conductivity enhancement of polymer/multiwalled carbon nanotube (MWCNT) composites by thermally-induced defunctionalization of MWCNTs. ACS Appl Mater Interfaces 2011;3:2204-2208.

[39] Zeng Y, Liu PF, Du JH, Zhao L, Ajayan PM, Cheng HM. Increasing the electrica conductivity of carbon nanotube/polymer composites by using weak nanotube-polymer interactions. Carbon 2010;48:3551-3558.

[40] Gazotti WA, Miceli GC, Geri A, Paoli, MA. A solid-state electrochromic device based on two optically complementary conducting polymers. Adv Mater 1998;10:60-64.

[41] Yu G, Pakbaz K, Heeger AJ. Optocoupler made from semiconducting polymers. J Electron Mater 1994;23: 925-928.

[42] Yu G, Wang J, McElvain J, Heeger AJ. Large-area, full-color image sensors made with semiconducting polymers. Adv Mater 1998;10:1431-1434.

[43] Frolov SV, Fujii A, Chinn D, Hirohata M, Hidayat R, Taraguchi M, Masuda T, Yoshino K, Vardeny ZV. Microlasers and micro-LEDs from disubstituted polyacetylene. Adv Mater 1998;10:869-872.

[44] Wang W, Schiff EA. Polyaniline on crystalline silicon heterojunction solar cells. Appl Phys Lett 2007;91:133504-3.

[45] Matsunaga T, Daifuku H, Nakajima T, Kawagoe T. Development of polyaniline–lithium secondary battery. Polym Adv Technol 1990;1:33-39.

[46] Scrosati B. Conducting polymers: Advanced materials for new design, rechargeable lithium batteries. Polym Int 1998;47:50-55.

[47] Wallace GG, Smyth M, Zhao H. Conducting electroactive polymer-based biosensors. Trends in Anal Chem 1999;18: 245-251.

[48] Li Y, Dong S. Electrochemically controlled release of adenosine 5 -triphosphate from polypyrrole film. J Chem Soc Chem Commun 1992;11: 827-828.

[49] Langsam N, Robeson LM. Substituted propyne polymers-part II. Effects of aging on the gas permeability properties of poly[1-(trimethylsilyl)propyne] for gas separation membranes Polym Eng Sci 1989;29:44-54.

[50] Arbizzani C, Mastragostino M, Meneghello L. Characterization by impedance spectroscopy of a polymer-based supercapacitor. Electrochim Acta 1995;40:2223-2228.

[51] Racicot R, Brown R, Yang SC. Corrosion protection of aluminum alloys by double-strand polyaniline. Synth Met 1997;85:1263-1264.

[52] Wessling B. Passivation of metals by coating with polyaniline: Corrosion potential shift and morphological changes. Adv Mater 1994;6:226-228.

[53] Katoh R, Furube A, Yoshihara T, Hara K, Fujihashi G, Takano S, Murata S, Arakawa H, Tachiya M. Efficiencies of electron injection from excited N_3 dye into nanocrystalline semiconductor (ZrO_2, TiO_2, ZnO, Nb_2O_5, SnO_2, In_2O_3) films. J Phys Chem B 2004;108:4818-4822.

[54] Letheby H. On the production of a blue substance by the electrolysis of sulphate of aniline. J Chem Soc 1862;15:161-163.

[55] Anilkumar P, Jayakannan M. New renewable resource amphiphilic molecular design

tor size-controlled and highly ordered polyaniline nanofibers. Langmuir 2006;22:5952-5957.

[56] Anilkumar P, Jayakannan M. Hydroxyl-functionalized polyaniline nanospheres: tracing molecular interactions at the nanosurface via vitamin c sensing. Langmuir 2008; 24:9754-9762.

[57] Li X, Zhang H, Wang G, Jiang Z. A novel electrode material based on a highly homogeneous polyaniline/titanium oxide hybrid for high-rate electrochemical capacitors. J Mater Chem 2010; 20:10598-10601.

[58] Cui G, Lee JS, Kim SJ, Nam H, Cha GS, Kim HD. Potentiometric pCO_2 sensor using polyaniline-coated pH-sensitive electrodes. Analyst 1998;123:1855-1859.

[59] Sivakumar C, Gopalan A, Vasudevan T, Wen TC. Kinetics of polymerization of N-methyl aniline using UV–VIS spectroscopy. Synth Met 2002;126:123-135.

[60] Gospodinova N, Terlemezyan L, Mokreva P, Kossev K. On the mechanism of oxidative polymerization of aniline. Polymer 1993;34:2434-2437.

[61] Gospodinova N, Terlemezyan L, Conducting polymers prepared by oxidative polymerization: polyaniline. Prog Polym Sci 1998;23:1443–1484.

[62] Hatchett DW, Josowicz M, Janata J. Acid doping of polyaniline: spectroscopic and electrochemical studies. J Phys Chem B 1999;103:10992-10998.

[63] Hatano M, Kambar S, Okamoto S. Paramagnetic and electric properties of polyacetylene. J Polym Sci 1961;51:S26-S29.

[64] Olio AD, Dassola G, Varacca G, Bocche V, Compt Rend (Paris) 1968;267C:433.

[65] Ceramic, Oxford English dictionary (3rd ed.). Oxford University Press. September 2005.

[66] Geiger G. Introduction To Ceramics. American Ceramic Society.

[67] Schadler LS, Ajayan PM (Eds.). Nanocomposite science and technology. Wiley-VCH Verlag 2003.

[68] Radhakrishnan VK, Davis EW, Davis VA. Influence of initial mixing methods on melt-extruded single-walled carbon nanotube–polypropylenenanocomposites. Polymer Engineering and Science 2010;50: 1831–1842.

[69] Ahmad MB, Gharayebi Y, Salit MS, Hussein ZM, Shameli K. Comparison of *in situ* polymerization and solution-dispersiontechniques in the preparation of

polyimide/montmorillonite (mmt) nanocomposites. Int J Mol Sci 2011;12:6040- 6050.

[70] Negrete-Herrera N *et al.* Synthesis of polymer/laponite nanocomposite latex particles via emulsion polymerization using silylated and cation-exchanged Laponite clay platelets. Progress in Solid State Chemistry 2006;34 :121-137.

[71] Ravve A. Kluwer academic publishers, New York, 2000.

[72] Kumar AP, Depan D, Tomer NS, Singh RP, Nanoscale particles for polymer degradation and stabilization-Trends and future perspectives. Prog Polym Sci 2009;34:479-515.

[73] Alariqi SAS, Kumar AP, Rao BSM, Singh RP. Stabilization of g-sterilized biomedical polyolefins by synergistic mixtures of oligomeric stabilizers. Part II. Polypropylene matrix. Polym Degrad Stab 2007;92:299-309.

[74] Rabek JF, Ranby B. Role of singlet oxygen in photo-oxidative degradation and photostabilization of polymers. Polym Eng Sci 1975;15:40-43.

[75] Klemchuk PP, Degradable plastics: A critical review. Polym Degrad Stab 1990;27:183-202.

[76] Baksi S, Basak P R, Biswas S, Nanocomposites -technology trends & application potential, Abstract

[77] Klemm D, Schumann D, Kramer F, Hessler N, Hornung M, Schmauder HP, Marsch S. Nanocelluloses as innovative polymers in research and application. In Klemm D (ed.) Polysaccharides II 2006;205:49-96.

[78] Klemm D, Kramer F, Moritz S, Lindstrom T, Ankerfors M, Gray D, Dorris A. Nanocelluloses: A new family of nature-based materials. Angew Chem Int Edit 2011;50:5438-5466.

[79] Wu ZS, Zhou G, Yin LC, Ren W, Li F, Cheng HM. Graphene/metal oxide composite electrode materials for energy storage. Nano Energy 2012;1:107–131.

[80] Chlupa Z, Flasara P, Kotojib A, Dlouhya I. Fracture behaviour of Al_2O_3/SiC nanocomposite ceramics after crack healing treatment, J Euro Cer Soc 2008;28:1073.

[81] Kothurkar NK. Solid state, transparent, cadmium sulfide-polyme nanocomposite, University of Florida 2004.

[82] Jabbour L, Gerbaldi C, Chaussy D, Zeno E, Bodoardod S, Beneventi D. Microfibrillated cellulose-graphite nanocomposites for highly flexible paper-like Li-ion

Battery electrodes. J Mater Chem 2010;20:7344.

[83] Barth RF, Coderre JA, Vicente MGH, Blue TE, Miyatake SI "Boron neutron capture therapy of brain tumors: current status and future prospects," in High-Grade Gliomas:Diagnosis and Treatment, G Barnett, Ed. Humana Press, Totowa, NJ, USA 2007;26:431.

[84] Rhim JW, Ng PK. Natural biopolymer-based nanocomposite films for.kaging applications. Crit Rev Food Sci Nutr. 2007;47(4):411-33.

Chapter 2

[1] Anwer T, Ansari MO, Mohammad F. Morphology and thermal stability of electrically conducting nanocomposites prepared by sulfosalicylic acid micelles assisted polymerization of aniline in presence of zro2 nanoparticles. Polymer-Plastics Technology and Engineering 2013;52:472–477.

[2] Ansari MO, Mohammad F. Thermal stability, electrical conductivity and ammonia sensing studies on p-toluenesulfonic acid doped polyaniline:titanium dioxide (pTSA/Pani:TiO2)nanocomposites. Sensors and Actuators B 2011;157:122-29.

[3] Anwer T, Ansari MO, Mohammad F. Dodecylbenzenesulfonic acid micelles assisted *in situ* preparation and enhanced thermoelectric performance of semiconducting polyaniline–zirconium oxide nanocomposites. Journal of Industrial and Engineering Chemistry 2013;191:653–1658.

Chapter 3

[1] Hatchett DW, Josowicz M, Janata J. Acid doping of polyaniline: spectroscopic and electrochemical studies. J Phys Chem B 1999;103:10992-10998.

[2] Ansari MO, Yadav SK, Cho JW, Mohammad F. Thermal stability in terms of DC electrical conductivity retention and efficacy of mixing technique in the preparation of nanocomposites of graphene/polyaniline over the carbon nanotubes/ polyaniline. Composites Part B: Engineering. 2013;47:155-161.

[3] Huang J, Kaner RB. A general chemical route to polyaniline nanofibers. J Amer Chem Soc 2004;126:851-855.

[4] Wang Y, Liu J, Tran HD, Mecklenburg M, Guan XN, Stieg A Z, Regan BC, Martin DC, Kaner RB. Morphological and Dimensional Control via Hierarchical Assembly of Doped Oligoaniline Single Crystals. Am Chem Soc 2012;134:9251−9262.

[5] Sathish M, Mitani S, Tomaia T, Honma I. MnO_2 assisted oxidative polymerization of aniline on graphene sheets: superior nanocomposite electrodes for electrochemical supercapacitors. J Mater Chem 2011;21:16216-16222.

[6] Zengin H, Zhou W, Jin J, Czerw R, Jr DWS, Echegoyen L, Carroll DL, Foulger SH. Carbon nanotube doped polyaniline. J Ballatoadvanced Materials 2002;14:1480-1483.

[7] Zhu ZZ, Wang Z, Li HL. Functional multi-walled carbon nanotube/polyaniline Composite films as supports of platinum for formic acid electrooxidation. Appl Surf Sci 2008;254:2934–40.

[8] Nagaraja M, Pattar J, Shashank N, Manjanna J, Kamada Y, Rajanna K, Mahesh HM. Electrical, structural and magnetic properties of polyaniline/pTSA-TiO_2 nanocomposites. Synth Met 2009;159:718-722.

[9] Ansari MO, Mohammad F Thermal stability of HCl-doped-polyaniline and TiO_2 nanoparticles-based nanocomposites. Journal of Applied Polymer Science 2012;124:4433-4442.